PEETER JOOT PEETERJOOT@PROTONMAIL.COM

QUANTUM MECHANICS II

QUANTUM MECHANICS II

PEETER JOOT PEETERJOOT@PROTONMAIL.COM

Notes and problems from UofT PHY456H1F 2012

November 2015 – version v.6

Peeter Joot peeterjoot@protonmail.com: *Quantum Mechanics II,* Notes and problems from UofT PHY456H1F 2012, © November 2015

COPYRIGHT

Copyright ©2015 Peeter Joot All Rights Reserved

This book may be reproduced and distributed in whole or in part, without fee, subject to the following conditions:

- The copyright notice above and this permission notice must be preserved complete on all complete or partial copies.
- Any translation or derived work must be approved by the author in writing before distribution.
- If you distribute this work in part, instructions for obtaining the complete version of this document must be included, and a means for obtaining a complete version provided.
- Small portions may be reproduced as illustrations for reviews or quotes in other works without this permission notice if proper citation is given.

Exceptions to these rules may be granted for academic purposes: Write to the author and ask.

Disclaimer: I confess to violating somebody's copyright when I copied this copyright statement.

DOCUMENT VERSION

Sources for this notes compilation can be found in the github repository
https://github.com/peeterjoot/physicsplay
The last commit (Nov/4/2015), associated with this pdf was
834e136b8e3635cc7ab824f3c74fcfdf8c6f909f

Dedicated to:
Aurora and Lance, my awesome kids, and
Sofia, who not only tolerates and encourages my studies, but is also awesome enough to think that math is sexy.

PREFACE

These are my personal lecture notes for the Fall 2011, University of Toronto Quantum mechanics II course (PHY456H1F), taught by Prof. John E Sipe.

The official description of this course was:

Quantum dynamics in Heisenberg and Schrodinger Pictures; WKB approximation; Variational Method; Time-Independent Perturbation Theory; Spin; Addition of Angular Momentum; Time-Dependent Perturbation Theory; Scattering.

This document contains a few things

- My lecture notes.

  Typos, if any, are probably mine (Peeter), and no claim nor attempt of spelling or grammar correctness will be made.

- Notes from reading of the text [4]. This may include observations, notes on what seem like errors, and some solved problems.

- Different ways of tackling some of the assigned problems than the solution sets.

- Some personal notes exploring details that were not clear to me from the lectures.

- Some worked problems.

Peeter Joot peeterjoot@protonmail.com

CONTENTS

Preface xi

I APPROXIMATE METHODS AND PERTUBATION 1

1 APPROXIMATE METHODS 3
- 1.1 Approximate methods for finding energy eigenvalues and eigenkets 3
- 1.2 Variational principle 4

2 PERTURBATION METHODS 13
- 2.1 States and wave functions 13
- 2.2 Excited states 16
- 2.3 Problems 17
  - 2.3.1 Helium atom ground state energy estimation 23
  - 2.3.2 Curious problem using the variational method to find the ground state energy of the Harmonic oscillator 26

3 TIME INDEPENDENT PERTURBATION THEORY 37
- 3.1 Time independent perturbation 40
- 3.2 Issues concerning degeneracy 45
- 3.3 Examples 54

4 TIME DEPENDENT PERTUBATION 57
- 4.1 Review of dynamics 57
- 4.2 Interaction picture 59
- 4.3 Justifying the Taylor expansion above (not class notes) 66
- 4.4 Recap: Interaction picture 69
- 4.5 Time dependent perturbation theory 71
- 4.6 Perturbation expansion 73
- 4.7 Time dependent perturbation 79
- 4.8 Sudden perturbations 81
- 4.9 Adiabatic perturbations 84
- 4.10 Adiabatic perturbation theory (cont.) 87
- 4.11 Examples 90

5 FERMI'S GOLDEN RULE 95
- 5.1 Recap. Where we got to on Fermi's golden rule 99
- 5.2 Fermi's Golden rule 100

6 WKB METHOD 107
- 6.1 WKB (Wentzel-Kramers-Brillouin) Method 107

6.2 Turning points. 111
6.3 Examples 112

ii SPIN, ANGULAR MOMENTUM, AND TWO PARTICLE SYSTEMS 117

7 COMPOSITE SYSTEMS 119
7.1 Hilbert Spaces 119
7.2 Operators 121
7.3 Generalizations 122
7.4 Recalling the Stern-Gerlach system from PHY354 122

8 SPIN AND SPINORS 125
8.1 Generators 125
8.2 Generalizations 130
8.3 Multiple wavefunction spaces 133

9 REPRESENTATION OF TWO STATE KETS AND PAULI SPIN MATRICES 139
9.1 Representation of kets 139
9.2 Representation of two state kets 144
9.3 Pauli spin matrices 144

10 ROTATION OPERATOR IN SPIN SPACE 147
10.1 Formal Taylor series expansion 147
10.2 Spin dynamics 150
10.3 The hydrogen atom with spin 153

11 TWO SPIN SYSTEMS, ANGULAR MOMENTUM, AND CLEBSCH-GORDON CONVENTION 157
11.1 Two spins 157
11.2 More on two spin systems 161
11.3 Recap: table of two spin angular momenta 166
11.4 Tensor operators 171

12 ROTATIONS OF OPERATORS AND SPHERICAL TENSORS 173
12.1 Setup 173
12.2 Infinitesimal rotations 174
12.3 A problem 175
12.4 How do we extract these buried simplicities? 175
12.5 Motivating spherical tensors 177
12.6 Spherical tensors (cont) 178

iii SCATTERING THEORY 183

13 SCATTERING THEORY 185
13.1 Setup 185
13.2 1D QM scattering. No potential wave packet time evolution 186
13.3 A Gaussian wave packet 188

13.4 With a potential 189
13.5 Considering the time independent case temporarily 191
13.6 Recap 193
14 3D SCATTERING 199
14.1 Setup 199
14.2 Seeking a post scattering solution away from the potential 200
14.3 The radial equation and its solution 202
14.4 Limits of spherical Bessel and Neumann functions 204
14.5 Back to our problem 204
14.6 Scattering geometry and nomenclature 206
14.7 Appendix 207
14.8 Verifying the solution to the spherical Bessel equation 210
14.9 Scattering cross sections 213
15 BORN APPROXIMATION 219

IV NOTES AND PROBLEMS 223
16 SIMPLE ENTANGLEMENT EXAMPLE 225
17 PROBLEM SET 4, PROBLEM 2 NOTES 227
18 A DIFFERENT DERIVATION OF THE ADIABATIC PERTURBATION COEFFICIENT EQUATION 233
19 SECOND ORDER TIME EVOLUTION FOR THE COEFFICIENTS OF AN INITIALLY PURE KET WITH AN ADIABATICALLY CHANGING HAMILTONIAN 237
20 DEGENERACY AND DIAGONALIZATION 243
20.1 Motivation 243
20.2 A four state Hamiltonian 243
20.3 Generalizing slightly 245
21 REVIEW OF APPROXIMATION RESULTS 251
21.1 Motivation 251
21.2 Variational method 251
21.3 Time independent perturbation 251
21.4 Degeneracy 252
21.5 Interaction picture 254
21.6 Time dependent perturbation 254
21.7 Sudden perturbations 255
21.8 Adiabatic perturbations 256
21.9 WKB 257
22 ON CONDITIONS FOR CLEBSH-GORDAN COEFFICIENTS TO BE ZERO 259
22.1 Motivation 259

22.2 Recap on notation 259
22.3 The J_z action 260
23 ONE MORE ADIABATIC PERTURBATION DERIVATION 261
23.1 Motivation 261
23.2 Build up 261
23.3 Adiabatic case 262
23.4 Summary 264
24 A SUPER SHORT DERIVATION OF THE TIME DEPENDENT PERTURBATION RESULT 267
25 SECOND FORM OF ADIABATIC APPROXIMATION 269

V APPENDICES 271
A HARMONIC OSCILLATOR REVIEW 273
B VERIFYING THE HELMHOLTZ GREEN'S FUNCTION 277
C EVALUATING THE SQUARED SINC INTEGRAL 283
D DERIVATIVE RECURRENCE RELATION FOR HERMITE POLYNOMIALS 287
E MATHEMATICA NOTEBOOKS 289

VI BIBLIOGRAPHY 293

BIBLIOGRAPHY 295

LIST OF FIGURES

Figure 1.1 qmTwoL2fig1 4
Figure 1.2 qmTwoL2fig2 6
Figure 1.3 qmTwoL2fig3 7
Figure 1.4 qmTwoL2fig4 8
Figure 1.5 qmTwoL2fig5 9
Figure 1.6 qmTwoL2fig6 10
Figure 2.1 Pictorial illustration of ket projections 14
Figure 2.2 Illustration of variation of energy with variation of Hamiltonian 15
Figure 2.3 Exponential trial function with absolute exponential die off 32
Figure 2.4 First ten orders, fitting harmonic oscillator wavefunctions to this trial function 33
Figure 2.5 Tenth order harmonic oscillator wavefunction fitting 33
Figure 2.6 stepFunction 34
Figure 3.1 Example of small perturbation from known Hamiltonian 38
Figure 3.2 Energy level splitting 56
Figure 4.1 Coulomb interaction of a nucleus and heavy atom 59
Figure 4.2 atom in a field 61
Figure 4.3 Perturbation around energy level s 74
Figure 4.4 Slow nucleus passing an atom 75
Figure 4.5 Fields for nucleus atom example 76
Figure 4.6 Atom interacting with an EM pulse 77
Figure 4.7 Positive and negative frequencies 80
Figure 4.8 Gaussian wave packet 80
Figure 4.9 FTgaussianWavePacket 81
Figure 4.10 Sudden step Hamiltonian 82
Figure 4.11 Harmonic oscillator sudden Hamiltonian perturbation 83
Figure 4.12 Energy level variation with time 89
Figure 4.13 Phase whipping around 90
Figure 4.14 Degenerate energy level splitting 91
Figure 5.1 Gaussian wave packet 96
Figure 5.2 Sine only after an initial time 96
Figure 5.3 ω_{mi} illustrated 97
Figure 5.4 FIXME: qmTwoL9fig7 98
Figure 5.5 Sine only after an initial time 99

Figure 5.6 Perturbation from i to mth energy levels 99
Figure 5.7 Two sinc lobes 101
Figure 5.8 Continuum of energy levels for ionized states of an atom 101
Figure 5.9 Semi-conductor well 101
Figure 5.10 103
Figure 5.11 Momentum space view 104
Figure 6.1 Finite well potential 107
Figure 6.2 Example of a general potential 111
Figure 6.3 Turning points where WKB will not work 112
Figure 6.4 Diagram for patching method discussion 112
Figure 6.5 Arbitrary potential in an infinite well 113
Figure 8.1 Vector translation 125
Figure 8.2 Active spatial translation 128
Figure 8.3 Active vector rotations 129
Figure 8.4 A example pair of non-commuting rotations 129
Figure 8.5 Rotated temperature (scalar) field 132
Figure 8.6 Rotating a capacitance electric field 133
Figure 10.1 Magnetic moment due to steady state current 150
Figure 10.2 Charge moving in circle 150
Figure 10.3 Induced torque in the presence of a magnetic field 151
Figure 10.4 Precession due to torque 152
Figure 11.1 Angular momentum triangle inequality 169
Figure 11.2 active rotation 171
Figure 11.3 Rotating a wavefunction 172
Figure 12.1 Rotating a state centered at F 173
Figure 13.1 classical collision of particles 185
Figure 13.2 Classical scattering radius and impact parameter 186
Figure 13.3 Wave packet for a particle wavefunction $\Re(\psi(x,0))$ 186
Figure 13.4 Gaussian wave packet 188
Figure 13.5 moving spreading Gaussian packet 189
Figure 13.6 QM wave packet prior to interaction with repulsive potential 189
Figure 13.7 QM wave packet long after interaction with repulsive potential 190
Figure 13.8 Kinetic energy greater than potential energy 190
Figure 13.9 qmTwoL21Fig9 191
Figure 13.10 potential zero outside of a specific region 192
Figure 13.11 A bounded positive potential 194
Figure 13.12 Wave packet in free space and with positive potential 195
Figure 13.13 Reflection and transmission of wave packet 195
Figure 14.1 Radially bounded spherical potential 199

Figure 14.2 Radially bounded potential 200
Figure 14.3 Scattering cross section 206
Figure 14.4 Bounded potential 213
Figure 14.5 plane wave front incident on particle 214
Figure 14.6 k space localized wave packet 215
Figure 14.7 point of measurement of scattering cross section 216
Figure 14.8 Plane wave vs packet wave front 218
Figure C.1 Contour distorted to one side of the double pole at the origin 283

Part I

APPROXIMATE METHODS AND PERTUBATION

1

APPROXIMATE METHODS

1.1 APPROXIMATE METHODS FOR FINDING ENERGY EIGENVALUES AND EIGENKETS

In many situations one has a Hamiltonian H

$$H|\Psi_{n\alpha}\rangle = E_n|\Psi_{n\alpha}\rangle \tag{1.1}$$

Here α is a "degeneracy index" (example: as in Hydrogen atom).

Why?

- Simplifies dynamics

  take

$$|\Psi(0)\rangle = \sum_{n\alpha}|\Psi_{n\alpha}\rangle\langle\Psi_{n\alpha}|\Psi(0)\rangle = \sum_{n\alpha}c_{n\alpha}|\Psi_{n\alpha}\rangle \tag{1.2}$$

  Then

$$\begin{aligned}|\Psi(t)\rangle &= e^{-iHt/\hbar}|\Psi(0)\rangle \\ &= \sum_{n\alpha}c_{n\alpha}e^{-iHt/\hbar}|\Psi_{n\alpha}\rangle \\ &= \sum_{n\alpha}c_{n\alpha}e^{-iE_nt/\hbar}|\Psi_{n\alpha}\rangle\end{aligned} \tag{1.3}$$

- "Applied field"' can often be thought of a driving the system from one eigenstate to another.

- Stat mech.

  In thermal equilibrium

$$\langle O\rangle = \frac{\sum_{n\alpha}\langle\Psi_{n\alpha}|O|\Psi_{n\alpha}\rangle e^{-\beta E_n}}{Z} \tag{1.4}$$

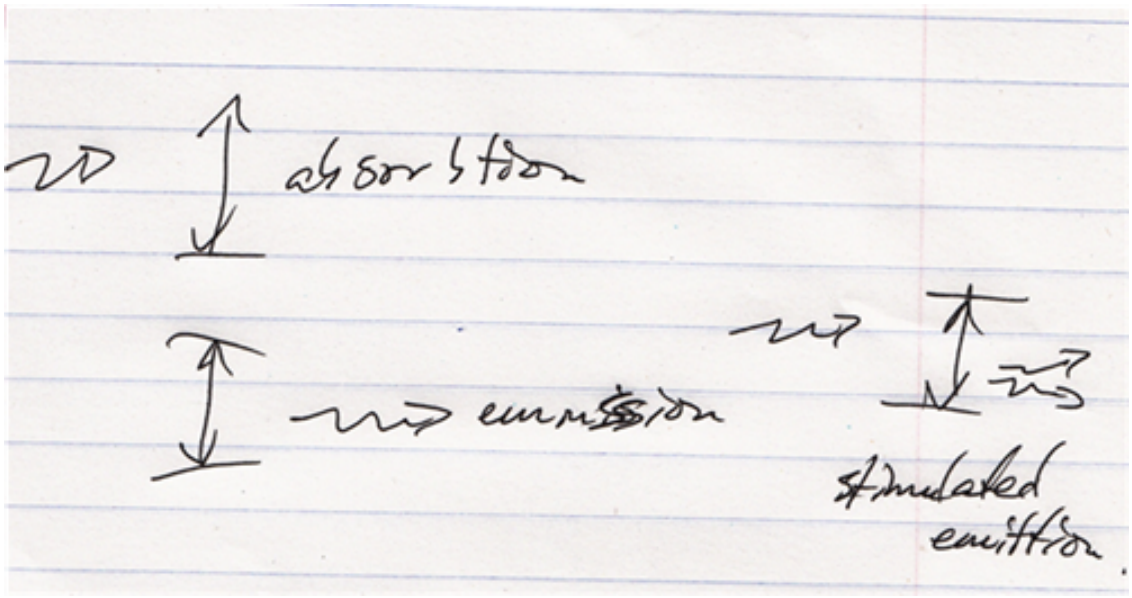

Figure 1.1: qmTwoL2fig1

where

$$\beta = \frac{1}{k_B T}, \tag{1.5}$$

and

$$Z = \sum_{n\alpha} e^{-\beta E_n} \tag{1.6}$$

1.2 VARIATIONAL PRINCIPLE

Consider any ket

$$|\Psi\rangle = \sum_{n\alpha} c_{n\alpha} |\Psi_{n\alpha}\rangle \tag{1.7}$$

(perhaps not even normalized), and where

$$c_{n\alpha} = \langle \Psi_{n\alpha} | \Psi \rangle \tag{1.8}$$

but we do not know these.

$$\langle \Psi | \Psi \rangle = \sum_{n\alpha} |c_{n\alpha}|^2 \tag{1.9}$$

$$\begin{aligned} \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} &= \frac{\sum_{n\alpha} |c_{n\alpha}|^2 E_n}{\sum_{m\beta} \left| c_{m\beta} \right|^2} \\ &\geq \frac{\sum_{n\alpha} |c_{n\alpha}|^2 E_0}{\sum_{m\beta} \left| c_{m\beta} \right|^2} \\ &= E_0 \end{aligned} \tag{1.10}$$

So for any ket we can form the upper bound for the ground state energy

$$\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0 \tag{1.11}$$

There is a whole set of strategies based on estimating the ground state energy. This is called the Variational principle for ground state. See §24.2 in the text [4].

We define the functional

$$E[\Psi] = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0 \tag{1.12}$$

If $|\Psi\rangle = c\,|\Psi_0\rangle$ where $|\Psi_0\rangle$ is the normalized ground state, then

$$E[c\Psi_0] = E_0 \tag{1.13}$$

Example 1.1: Hydrogen atom

$$\langle \mathbf{r} | H \left| \mathbf{r}' \right\rangle = \mathcal{H} \delta^3(\mathbf{r} - \mathbf{r}') \tag{1.14}$$

where

$$\mathcal{H} = -\frac{\hbar^2}{2\mu} \boldsymbol{\nabla}^2 - \frac{e^2}{r} \tag{1.15}$$

Here μ is the reduced mass.

We know the exact solution:

$$H|\Psi_0\rangle \tag{1.16}$$

$$E_0 = -R_y \tag{1.17}$$

$$R_y = \frac{\mu e^4}{2\hbar^2} \approx 13.6\text{eV} \tag{1.18}$$

$$\langle \mathbf{r}|\Psi_0\rangle = \Phi_{100}(\mathbf{r}) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0} \tag{1.19}$$

$$a_0 = \frac{\hbar^2}{\mu e^2} \approx 0.53\text{Å} \tag{1.20}$$

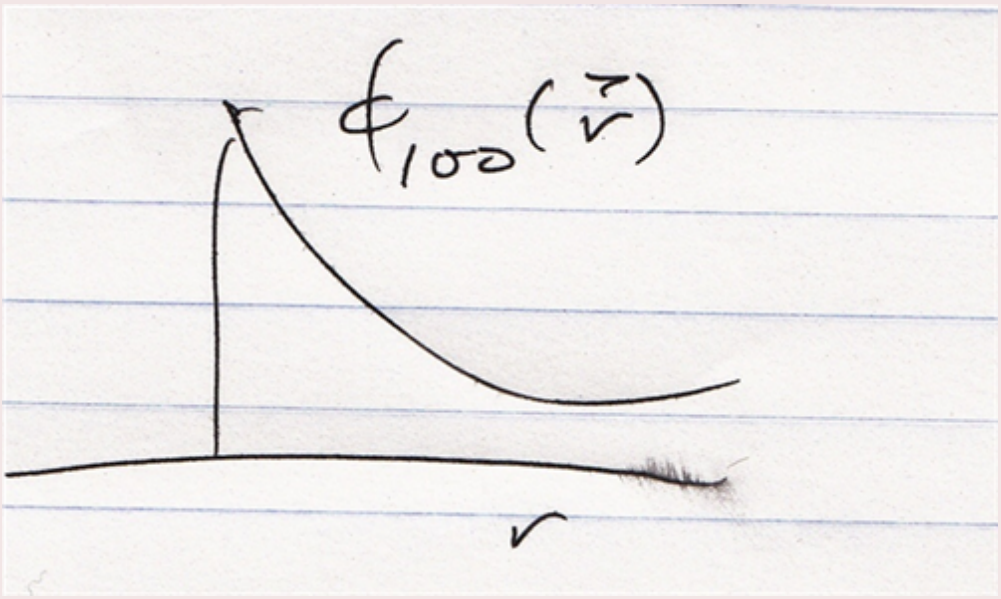

Figure 1.2: qmTwoL2fig2

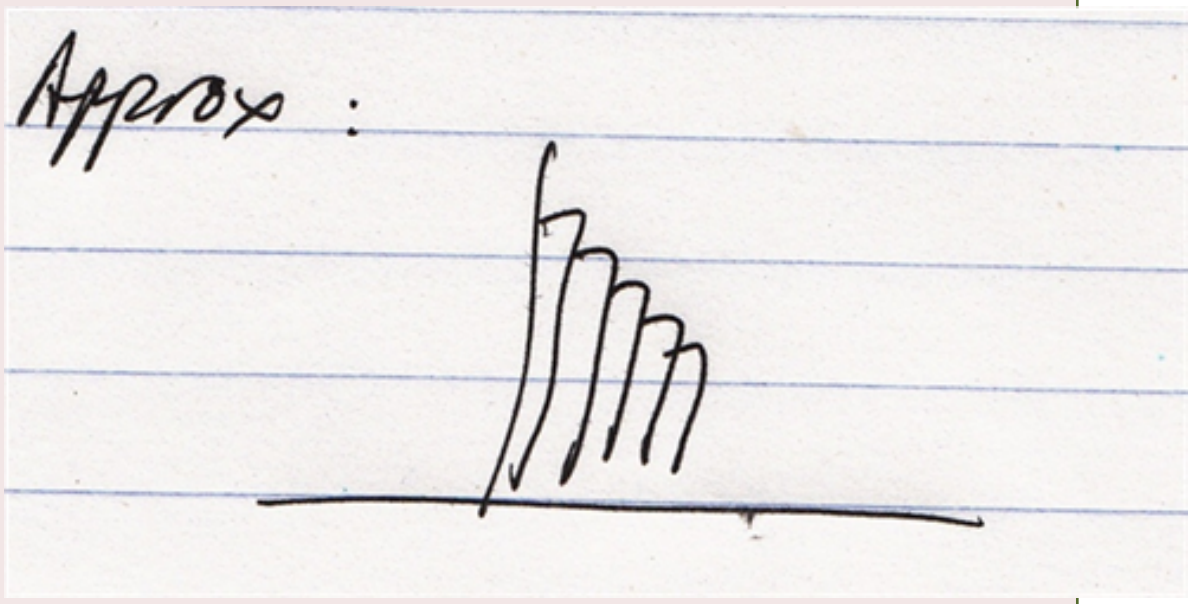

Figure 1.3: qmTwoL2fig3

estimate

$$\langle \Psi | H | \Psi \rangle = \int d^3\mathbf{r} \Psi^*(\mathbf{r}) \left(-\frac{\hbar^2}{2\mu} \boldsymbol{\nabla}^2 - \frac{e^2}{r} \right) \Psi(\mathbf{r})$$
$$\langle \Psi | \Psi \rangle = \int d^3\mathbf{r} |\Psi(\mathbf{r})|^2 \tag{1.21}$$

Or guess shape

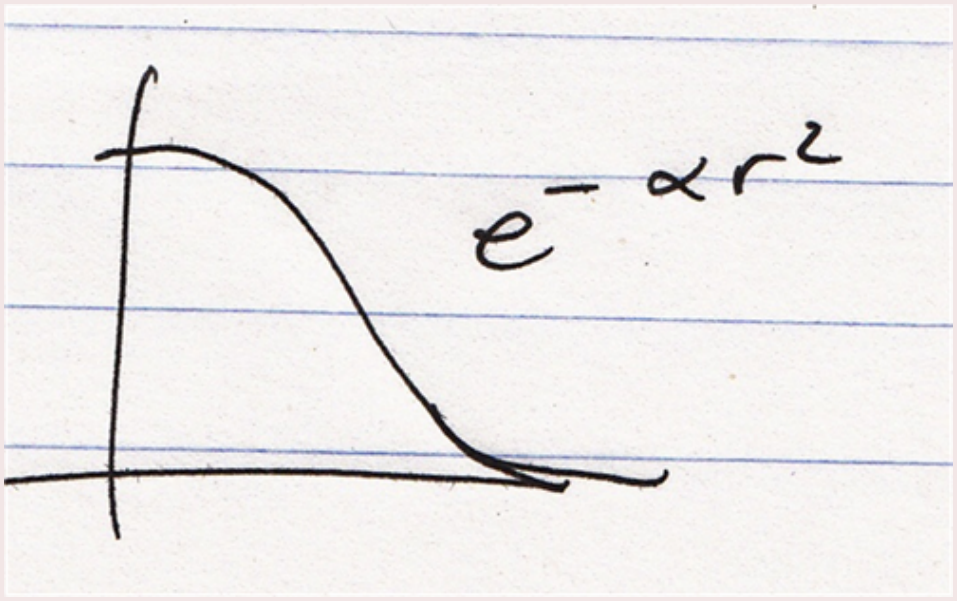

Figure 1.4: qmTwoL2fig4

Using the trial wave function $e^{-\alpha r^2}$

$$E[\Psi] \to E(\alpha) \tag{1.22}$$

$$E(\alpha) = \frac{\int d^3\mathbf{r} e^{-\alpha r^2}\left(-\frac{\hbar^2}{2\mu}\boldsymbol{\nabla}^2 - \frac{e^2}{r}\right)e^{-\alpha r^2}}{\int d^3\mathbf{r} e^{-2\alpha r^2}} \tag{1.23}$$

find

$$E(\alpha) = A\alpha - B\alpha^{1/2} \tag{1.24}$$

$$\begin{aligned} A &= \frac{3\hbar^2}{2\mu} \\ B &= 2e^2\left(\frac{2}{\pi}\right)^{1/2} \end{aligned} \tag{1.25}$$

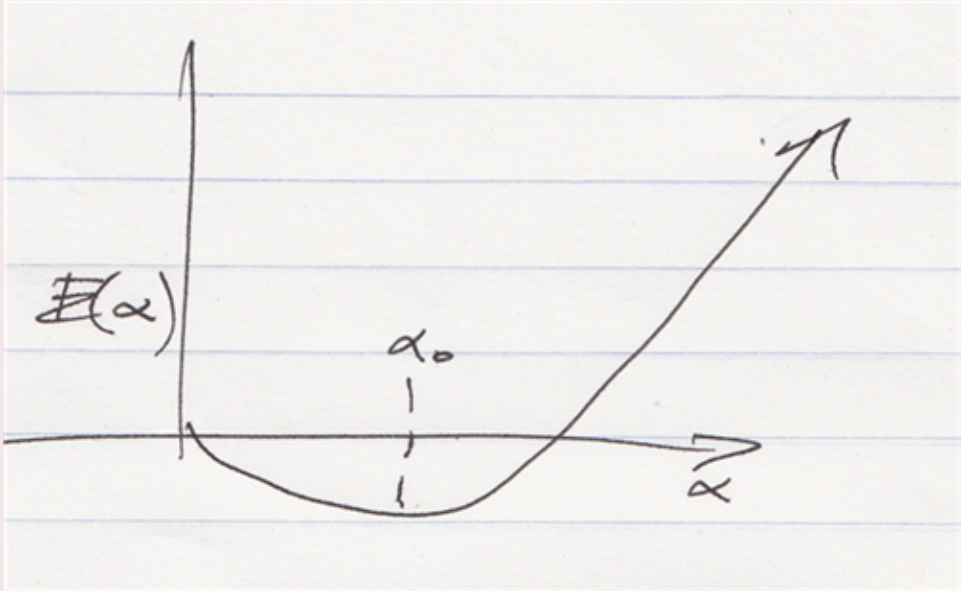

Figure 1.5: qmTwoL2fig5

Minimum at

$$\alpha_0 = \left(\frac{\mu e^2}{\hbar^2}\right)\frac{8}{9\pi} \tag{1.26}$$

So

$$E(\alpha_0) = -\frac{\mu e^4}{2\hbar^2}\frac{8}{3\pi} = -0.85R_y \tag{1.27}$$

maybe not too bad...

Example 1.2: Helium atom

Assume an infinite nuclear mass with nucleus charge $2e$

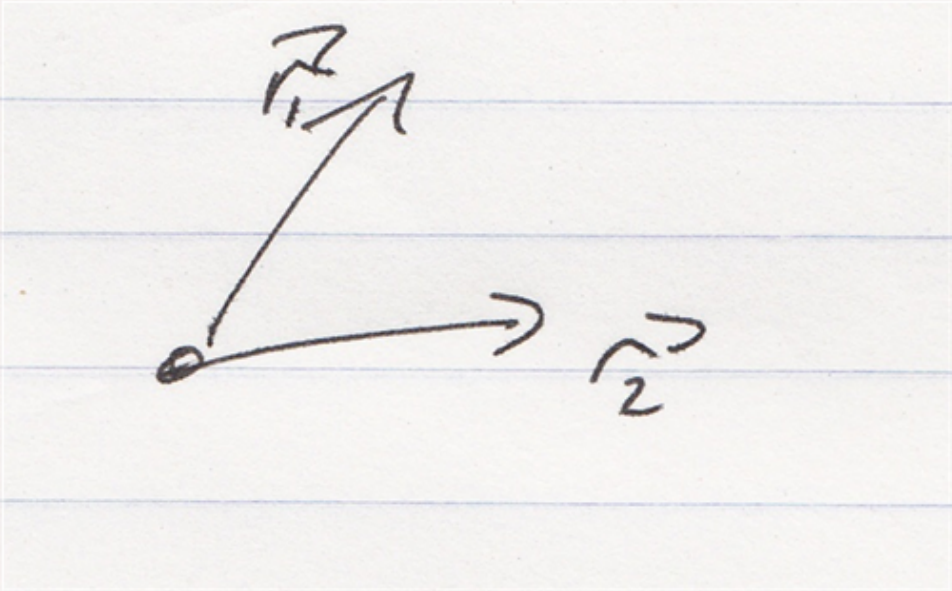

Figure 1.6: qmTwoL2fig6

ground state wavefunction

$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2) \tag{1.28}$$

The problem that we want to solve is

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e}{r} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\right)\Psi_0(\mathbf{r}_1, \mathbf{r}_2) = E_0\Psi_0(\mathbf{r}_1, \mathbf{r}_2) \tag{1.29}$$

Nobody can solve this problem. It is one of the simplest real problems in QM that cannot be solved exactly.

Suppose that we neglected the electron, electron repulsion. Then

$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2) = \overline{\Phi}_{100}(\mathbf{r}_1)\overline{\Phi}_{100}(\mathbf{r}_2) \tag{1.30}$$

where

$$\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 - \frac{2e}{r}\right)\overline{\Phi}_{100}(\mathbf{r}) = \epsilon\overline{\Phi}_{100}(\mathbf{r}) \tag{1.31}$$

with

$$\epsilon = -4R_y \tag{1.32}$$

$$R_y = \frac{me^4}{2\hbar^2} \tag{1.33}$$

This is the solution to

$$\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}_1^2 - \frac{\hbar^2}{2m}\boldsymbol{\nabla}_2^2 - \frac{2e}{r}\right)\Psi_0^{(0)}(\mathbf{r}_1,\mathbf{r}_2) = E_0\Psi_0(\mathbf{r}_1,\mathbf{r}_2) = E_0^{(0)}\Psi_0^{(0)}(\mathbf{r}_1,\mathbf{r}_2) \tag{1.34}$$

$$E_0^{(0)} = -8R_y. \tag{1.35}$$

Now we want to put back in the electron electron repulsion, and make an estimate.
Trial wavefunction

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,Z) = \left(\left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr_1/a_0}\right)\left(\left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr_2/a_0}\right) \tag{1.36}$$

expect that the best estimate is for $Z \in [1,2]$.
This can be calculated numerically, and we find

$$E(Z) = 2R_Y\left(Z^2 - 4Z + \frac{5}{8}Z\right) \tag{1.37}$$

The Z^2 comes from the kinetic energy. The $-4Z$ is the electron nuclear attraction, and the final term is from the electron-electron repulsion.

The actual minimum is

$$Z = 2 - \frac{5}{16} \tag{1.38}$$

$$E(2 - 5/16) = -77.5\text{eV} \tag{1.39}$$

Whereas the measured value is -78.6eV.

2

PERTURBATION METHODS

2.1 STATES AND WAVE FUNCTIONS

Suppose we have the following non-degenerate energy eigenstates

$$\begin{aligned} &\vdots \\ E_1 &\sim |\psi_1\rangle \\ E_0 &\sim |\psi_0\rangle \end{aligned} \tag{2.1}$$

and consider a state that is "very close" to $|\psi_n\rangle$.

$$|\psi\rangle = |\psi_n\rangle + |\delta\psi_n\rangle \tag{2.2}$$

We form projections onto $|\psi_n\rangle$ "direction". The difference from this projection will be written $|\psi_{n\perp}\rangle$, as depicted in fig. 2.1. This illustration cannot not be interpreted literally, but illustrates the idea nicely.

For the amount along the projection onto $|\psi_n\rangle$ we write

$$\langle\psi_n|\delta\psi_n\rangle = \delta\alpha \tag{2.3}$$

so that the total deviation from the original state is

$$|\delta\psi_n\rangle = \delta\alpha\,|\psi_n\rangle + |\delta\psi_{n\perp}\rangle\,. \tag{2.4}$$

The varied ket is then

$$|\psi\rangle = (1+\delta\alpha)\,|\psi_n\rangle + |\delta\psi_{n\perp}\rangle \tag{2.5}$$

where

$$(\delta\alpha)^2, \langle\delta\psi_{n\perp}|\delta\psi_{n\perp}\rangle \ll 1 \tag{2.6}$$

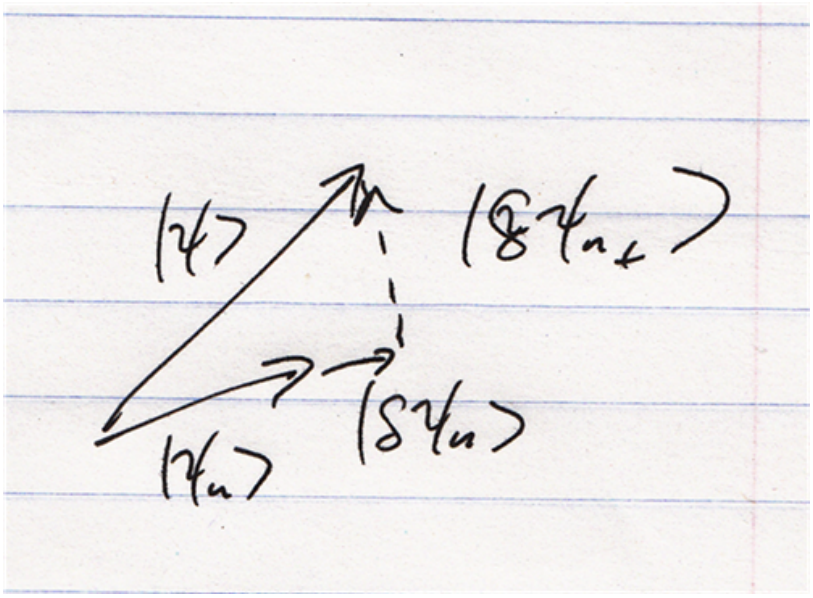

Figure 2.1: Pictorial illustration of ket projections

In terms of these projections our kets magnitude is

$$\begin{aligned}\langle\psi|\psi\rangle &= \big((1+\delta\alpha^*)\langle\psi_n| + \langle\delta\psi_{n\perp}|\big)\big((1+\delta\alpha)|\psi_n\rangle + |\delta\psi_{n\perp}\rangle\big)\\ &= |1+\delta\alpha|^2\langle\psi_n|\psi_n\rangle + \langle\delta\psi_{n\perp}|\delta\psi_{n\perp}\rangle\\ &\quad + (1+\delta\alpha^*)\langle\psi_n|\delta\psi_{n\perp}\rangle + (1+\delta\alpha)\langle\delta\psi_{n\perp}|\delta\psi_n\rangle\end{aligned} \tag{2.7}$$

Because $\langle\delta\psi_{n\perp}|\delta\psi_n\rangle = 0$ this is

$$\langle\psi|\psi\rangle = |1+\delta\alpha|^2\langle\delta\psi_{n\perp}|\delta\psi_{n\perp}\rangle\,. \tag{2.8}$$

Similarly for the energy expectation we have

$$\begin{aligned}\langle\psi|\psi\rangle &= \big((1+\delta\alpha^*)\langle\psi_n| + \langle\delta\psi_{n\perp}|\big)H\big((1+\delta\alpha)|\psi_n\rangle + |\delta\psi_{n\perp}\rangle\big)\\ &= |1+\delta\alpha|^2 E_n\langle\psi_n|\psi_n\rangle + \langle\delta\psi_{n\perp}|H\rangle\,\delta\psi_{n\perp}\\ &\quad + (1+\delta\alpha^*)E_n\langle\psi_n|\delta\psi_{n\perp}\rangle + (1+\delta\alpha)E_n\langle\delta\psi_{n\perp}|\delta\psi_n\rangle\end{aligned} \tag{2.9}$$

Or

$$\langle\psi|\,H\,|\psi\rangle = E_n|1+\delta\alpha|^2 + \langle\delta\psi_{n\perp}|\,H\,|\delta\psi_{n\perp}\rangle\,. \tag{2.10}$$

This gives

$$\begin{aligned} E[\psi] &= \frac{\langle\psi| H |\psi\rangle}{\langle\psi|\psi\rangle} \\ &= \frac{E_n|1+\delta\alpha|^2 + \langle\delta\psi_{n\perp}| H |\delta\psi_{n\perp}\rangle}{|1+\delta\alpha|^2 \langle\delta\psi_{n\perp}|\delta\psi_{n\perp}\rangle} \\ &= \frac{E_n + \frac{\langle\delta\psi_{n\perp}|H|\delta\psi_{n\perp}\rangle}{|1+\delta\alpha|^2}}{1 + \frac{\langle\delta\psi_{n\perp}|\delta\psi_{n\perp}\rangle}{|1+\delta\alpha|^2}} \\ &= E_n\left(1 - \frac{\langle\delta\psi_{n\perp}|\delta\psi_{n\perp}\rangle}{|1+\delta\alpha|^2} + \cdots\right) + \cdots \\ &= E_n\left[1 + O\left((\delta\psi_{n\perp})^2\right)\right] \end{aligned} \tag{2.11}$$

where

$$(\delta\psi_{n\perp})^2 \sim \langle\delta\psi_{n\perp}|\delta\psi_{n\perp}\rangle \tag{2.12}$$

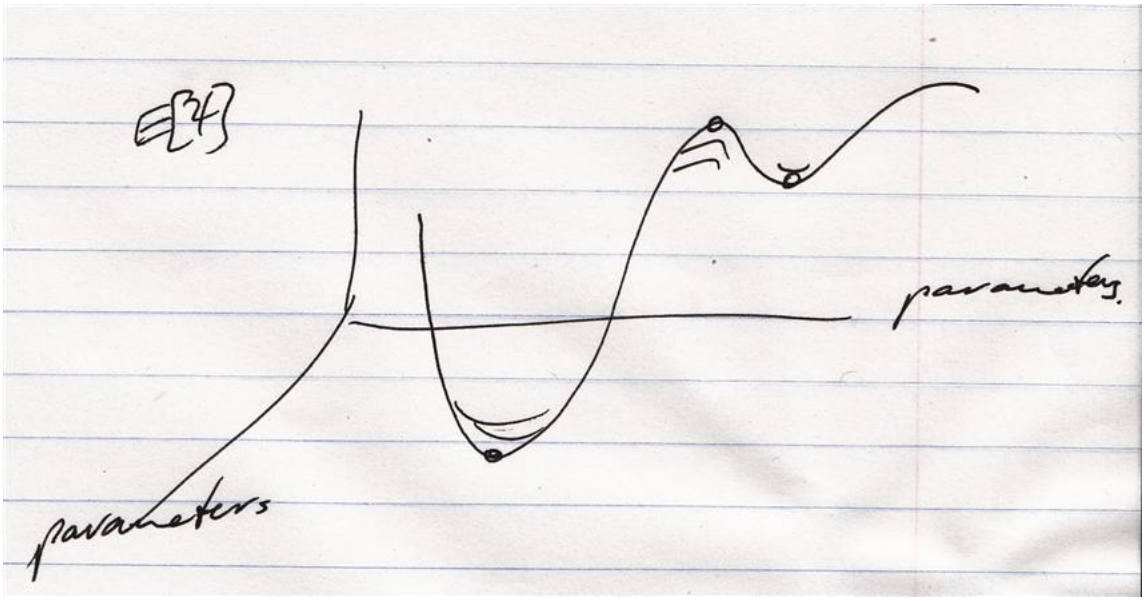

Figure 2.2: Illustration of variation of energy with variation of Hamiltonian

"small errors" in $|\psi\rangle$ do not lead to large errors in $E[\psi]$

It is reasonably easy to get a good estimate and E_0, although it is reasonably hard to get a good estimate of $|\psi_0\rangle$. This is for the same reason, because $E[]$ is not terribly sensitive.

2.2 EXCITED STATES

$$\begin{aligned} &\vdots \\ E_2 &\sim |\psi_2\rangle \\ E_1 &\sim |\psi_1\rangle \\ E_0 &\sim |\psi_0\rangle \end{aligned} \tag{2.13}$$

Suppose we wanted an estimate of E_1. If we knew the ground state $|\psi_0\rangle$. For any trial $|\psi\rangle$ form

$$\left|\psi'\right\rangle = |\psi\rangle - |\psi_0\rangle \langle\psi_0|\psi\rangle \tag{2.14}$$

We are taking out the projection of the ground state from an arbitrary trial function.
For a state written in terms of the basis states, allowing for an α degeneracy

$$|\psi\rangle = c_0 |\psi_0\rangle + \sum_{n>0,\alpha} c_{n\alpha} |\psi_{n\alpha}\rangle \tag{2.15}$$

$$\langle\psi_0|\psi\rangle = c_0 \tag{2.16}$$

and

$$\left|\psi'\right\rangle = \sum_{n>0,\alpha} c_{n\alpha} |\psi_{n\alpha}\rangle \tag{2.17}$$

(note that there are some theorems that tell us that the ground state is generally non-degenerate).

$$\begin{aligned} E[\psi'] &= \frac{\langle\psi'| H |\psi'\rangle}{\langle\psi'|\psi'\rangle} \\ &= \frac{\sum_{n>0,\alpha} |c_{n\alpha}|^2 E_n}{\sum_{m>0,\beta} \left|c_{m\beta}\right|^2} \geq E_1 \end{aligned} \tag{2.18}$$

Often do not know the exact ground state, although we might have a guess $\left|\tilde{\psi}_0\right\rangle$.
for

$$\left|\psi''\right\rangle = |\psi\rangle - \left|\tilde{\psi}_0\right\rangle \left\langle\tilde{\psi}_0|\psi\right\rangle \tag{2.19}$$

but cannot prove that

$$\frac{\langle\psi''|\, H\,|\psi''\rangle}{\langle\psi''|\psi''\rangle} \geq E_1 \tag{2.20}$$

Then
FIXME: missed something here.

$$\frac{\langle\psi'''|\, H\,|\psi'''\rangle}{\langle\psi'''|\psi'''\rangle} \geq E_1 \tag{2.21}$$

Somewhat remarkably, this is often possible. We talked last time about the Hydrogen atom. In that case, you can guess that the excited state is in the $2s$ orbital and and therefore orthogonal to the $1s$ (?) orbital.

2.3 PROBLEMS

Exercise 2.1 Harmonic oscillator (*2011 ps1/p1*)

Let H_o indicate the Hamiltonian of a 1D harmonic oscillator with mass m and frequency ω

$$H_o = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2 \tag{2.22}$$

and denote the energy eigenstates by $|n\rangle$, where n is the eigenvalue of the number operator.

1. Find $\langle n|\, X^4\,|n\rangle$
2. Quadratic pertubation
   Find the ground state energy of the Hamiltonian $H = H_o + \gamma X^2$. You may assume $\gamma > 0$. [Hint: This is not a trick question.]
3. linear pertubation
   Find the ground state energy of the Hamiltonian $H = H_o - \alpha X$. [Hint: This is a bit harder than part 2 but not much. Try "completing the square."]

Answer for Exercise 2.1

Part 1. X^4 Working through A we have now got enough context to attempt the first part of the question, calculation of

$$\langle n|\, X^4\,|n\rangle \tag{2.23}$$

We have calculated things like this before, such as

$$\langle n| X^2 |n\rangle = \frac{\hbar}{2m\omega} \langle n| (a + a^\dagger)^2 |n\rangle \tag{2.24}$$

To continue we need an exact relation between $|n\rangle$ and $|n \pm 1\rangle$. Recall that $a|n\rangle$ was an eigenstate of $a^\dagger a$ with eigenvalue $n - 1$. This implies that the eigenstates $a|n\rangle$ and $|n - 1\rangle$ are proportional

$$a|n\rangle = c_n |n - 1\rangle , \tag{2.25}$$

or

$$\begin{aligned} \langle n| a^\dagger a |n\rangle &= |c_n|^2 \langle n - 1|n - 1\rangle = |c_n|^2 \\ n \langle n|n\rangle &= \\ n &= \end{aligned} \tag{2.26}$$

so that

$$a|n\rangle = \sqrt{n} |n - 1\rangle . \tag{2.27}$$

Similarly let

$$a^\dagger |n\rangle = b_n |n + 1\rangle , \tag{2.28}$$

or

$$\begin{aligned} \langle n| aa^\dagger |n\rangle &= |b_n|^2 \langle n - 1|n - 1\rangle = |b_n|^2 \\ \langle n| (1 + a^\dagger a) |n\rangle &= \\ 1 + n &= \end{aligned} \tag{2.29}$$

so that

$$a^\dagger |n\rangle = \sqrt{n + 1} |n + 1\rangle . \tag{2.30}$$

We can now return to eq. (2.23), and find

$$\langle n| X^4 |n\rangle = \frac{\hbar^2}{4m^2\omega^2} \langle n| (a + a^\dagger)^4 |n\rangle \tag{2.31}$$

Consider half of this braket

$$\begin{aligned}(a+a^\dagger)^2\,|n\rangle &= \left(a^2+(a^\dagger)^2+a^\dagger a+aa^\dagger\right)|n\rangle \\ &= \left(a^2+(a^\dagger)^2+a^\dagger a+(1+a^\dagger a)\right)|n\rangle \\ &= \left(a^2+(a^\dagger)^2+1+2a^\dagger a\right)|n\rangle \\ &= \sqrt{n-1}\,\sqrt{n-2}\,|n-2\rangle+\sqrt{n+1}\,\sqrt{n+2}\,|n+2\rangle+|n\rangle+2n\,|n\rangle\end{aligned} \tag{2.32}$$

Squaring, utilizing the Hermitian nature of the X operator

$$\langle n|\,X^4\,|n\rangle = \frac{\hbar^2}{4m^2\omega^2}\left((n-1)(n-2)+(n+1)(n+2)+(1+2n)^2\right) = \frac{\hbar^2}{4m^2\omega^2}\left(6n^2+4n+5\right) \tag{2.33}$$

Part 2. Quadratic ground state Find the ground state energy of the Hamiltonian $H = H_0 + \gamma X^2$ for $\gamma > 0$.

The new Hamiltonian has the form

$$H = \frac{P^2}{2m}+\frac{1}{2}m\left(\omega^2+\frac{2\gamma}{m}\right)X^2 = \frac{P^2}{2m}+\frac{1}{2}m\omega'^2X^2, \tag{2.34}$$

where

$$\omega' = \sqrt{\omega^2+\frac{2\gamma}{m}} \tag{2.35}$$

The energy states of the Hamiltonian are thus

$$E_n = \hbar\sqrt{\omega^2+\frac{2\gamma}{m}}\left(n+\frac{1}{2}\right) \tag{2.36}$$

and the ground state of the modified Hamiltonian H is thus

$$E_0 = \frac{\hbar}{2}\sqrt{\omega^2+\frac{2\gamma}{m}} \tag{2.37}$$

Part 3. Linear ground state Find the ground state energy of the Hamiltonian $H = H_0 - \alpha X$.

With a bit of play, this new Hamiltonian can be factored into

$$H = \hbar\omega\left(b^\dagger b+\frac{1}{2}\right)-\frac{\alpha^2}{2m\omega^2} = \hbar\omega\left(bb^\dagger-\frac{1}{2}\right)-\frac{\alpha^2}{2m\omega^2}, \tag{2.38}$$

where

$$\begin{aligned} b &= \sqrt{\frac{m\omega}{2\hbar}} X + \frac{iP}{\sqrt{2m\hbar\omega}} - \frac{\alpha}{\omega\sqrt{2m\hbar\omega}} \\ b^\dagger &= \sqrt{\frac{m\omega}{2\hbar}} X - \frac{iP}{\sqrt{2m\hbar\omega}} - \frac{\alpha}{\omega\sqrt{2m\hbar\omega}}. \end{aligned} \tag{2.39}$$

From eq. (2.38) we see that we have the same sort of commutator relationship as in the original Hamiltonian

$$\left[b, b^\dagger\right] = 1, \tag{2.40}$$

and because of this, all the preceding arguments follow unchanged with the exception that the energy eigenstates of this Hamiltonian are shifted by a constant

$$H|n\rangle = \left(\hbar\omega\left(n + \frac{1}{2}\right) - \frac{\alpha^2}{2m\omega^2}\right)|n\rangle, \tag{2.41}$$

where the $|n\rangle$ states are simultaneous eigenstates of the $b^\dagger b$ operator

$$b^\dagger b|n\rangle = n|n\rangle. \tag{2.42}$$

The ground state energy is then

$$E_0 = \frac{\hbar\omega}{2} - \frac{\alpha^2}{2m\omega^2}. \tag{2.43}$$

This makes sense. A translation of the entire position of the system should not effect the energy level distribution of the system, but we have set our reference potential differently, and have this constant energy adjustment to the entire system.

Exercise 2.2 Expectation values for position operators for spinless hydrogen (*2011 ps1/p2*)

Show that for all energy eigenstates $|\Phi_{nlm}\rangle$ of the (spinless) hydrogen atom, where as usual n, l, and m are respectively the principal, azimuthal, and magnetic quantum numbers, we have

$$\langle\Phi_{nlm}|X|\Phi_{nlm}\rangle = \langle\Phi_{nlm}|Y|\Phi_{nlm}\rangle = \langle\Phi_{nlm}|Z|\Phi_{nlm}\rangle = 0 \tag{2.44}$$

[Hint: Take note of the parity of the spherical harmonics (see "quick summary" notes on the spherical harmonics).]

Answer for Exercise 2.2

The summary sheet provides us with the wavefunction

$$\langle \mathbf{r}|\Phi_{nlm}\rangle = \frac{2}{n^2 a_0^{3/2}}\sqrt{\frac{(n-l-1)!}{(n+l)!\,)^3}}F_{nl}\left(\frac{2r}{na_0}\right)Y_l^m(\theta,\phi), \tag{2.45}$$

where F_{nl} is a real valued function defined in terms of Lagueere polynomials. Working with the expectation of the X operator to start with we have

$$\begin{aligned}
\langle \Phi_{nlm}|\, X\,|\Phi_{nlm}\rangle &= \int \langle \Phi_{nlm}|\mathbf{r}'\rangle \langle \mathbf{r}'|\, X\,|\mathbf{r}\rangle \langle \mathbf{r}|\Phi_{nlm}\rangle\, d^3\mathbf{r}d^3\mathbf{r}' \\
&= \int \langle \Phi_{nlm}|\mathbf{r}'\rangle\, \delta(\mathbf{r}-\mathbf{r}')r\sin\theta\cos\phi\, \langle \mathbf{r}|\Phi_{nlm}\rangle\, d^3\mathbf{r}d^3\mathbf{r}' \\
&= \int \Phi^*_{nlm}(\mathbf{r})r\sin\theta\cos\phi\Phi_{nlm}(\mathbf{r})d^3\mathbf{r} \\
&\sim \int r^2 dr\left|F_{nl}\left(\frac{2r}{na_0}\right)\right|^2 r\int \sin\theta d\theta d\phi Y_l^{m*}(\theta,\phi)\sin\theta\cos\phi Y_l^m(\theta,\phi)
\end{aligned} \tag{2.46}$$

Recalling that the only ϕ dependence in Y_l^m is $e^{im\phi}$ we can perform the $d\phi$ integration directly, which is

$$\int_{\phi=0}^{2\pi}\cos\phi d\phi e^{-im\phi}e^{im\phi} = 0. \tag{2.47}$$

We have the same story for the Y expectation which is

$$\langle \Phi_{nlm}|\, X\,|\Phi_{nlm}\rangle \sim \int r^2 dr\left|F_{nl}\left(\frac{2r}{na_0}\right)\right|^2 r\int \sin\theta d\theta d\phi Y_l^{m*}(\theta,\phi)\sin\theta\sin\phi Y_l^m(\theta,\phi). \tag{2.48}$$

Our ϕ integral is then just

$$\int_{\phi=0}^{2\pi}\sin\phi d\phi e^{-im\phi}e^{im\phi} = 0, \tag{2.49}$$

also zero. The Z expectation is a slightly different story. There we have

$$\begin{aligned}
\langle \Phi_{nlm}|\, Z\,|\Phi_{nlm}\rangle \sim &\int dr\left|F_{nl}\left(\frac{2r}{na_0}\right)\right|^2 r^3 \\
&\int_0^{2\pi} d\phi\int_0^{\pi}\sin\theta d\theta\,(\sin\theta)^{-2m}\left(\frac{d^{l-m}}{d(\cos\theta)^{l-m}}\sin^{2l}\theta\right)^2\cos\theta.
\end{aligned} \tag{2.50}$$

Within this last integral we can make the substitution

$$\begin{aligned} u &= \cos\theta \\ \sin\theta d\theta &= -d(\cos\theta) = -du \\ u &\in [1,-1], \end{aligned} \tag{2.51}$$

and the integral takes the form

$$-\int_{-1}^{1}(-du)\frac{1}{(1-u^2)^m}\left(\frac{d^{l-m}}{du^{l-m}}(1-u^2)^l\right)^2 u. \tag{2.52}$$

Here we have the product of two even functions, times one odd function (u), over a symmetric interval, so the end result is zero, completing the problem.

I was not able to see how to exploit the parity result suggested in the problem, but it was not so bad to show these directly.

Exercise 2.3 Angular momentum operator

2011 ps1/p3

Working with the appropriate expressions in *Cartesian components, confirm that* $L_i|\psi\rangle = 0$ *for each component of angular momentum* L_i*, if* $\langle \mathbf{r}|\psi\rangle = \psi(\mathbf{r})$ *is in fact only a function of* $r = |\mathbf{r}|$.

Answer for Exercise 2.3

In order to proceed, we will have to consider a matrix element, so that we can operate on $|\psi\rangle$ in position space. For that matrix element, we can proceed to insert complete states, and reduce the problem to a question of wavefunctions. That is

$$\begin{aligned} \langle \mathbf{r}|L_i|\psi\rangle &= \int d^3\mathbf{r}'\,\langle \mathbf{r}|L_i\left|\mathbf{r}'\right\rangle\langle \mathbf{r}'\left|\psi\right\rangle \\ &= \int d^3\mathbf{r}'\,\langle \mathbf{r}|\epsilon_{iab}X_aP_b\left|\mathbf{r}'\right\rangle\langle \mathbf{r}'\left|\psi\right\rangle \\ &= -i\hbar\epsilon_{iab}\int d^3\mathbf{r}'\,x_a\langle \mathbf{r}|\frac{\partial\psi(\mathbf{r}')}{\partial X_b}\left|\mathbf{r}'\right\rangle \\ &= -i\hbar\epsilon_{iab}\int d^3\mathbf{r}'\,x_a\frac{\partial\psi(\mathbf{r}')}{\partial x_b}\langle \mathbf{r}\left|\mathbf{r}'\right\rangle \\ &= -i\hbar\epsilon_{iab}\int d^3\mathbf{r}'\,x_a\frac{\partial\psi(\mathbf{r}')}{\partial x_b}\delta^3(\mathbf{r}-\mathbf{r}') \\ &= -i\hbar\epsilon_{iab}x_a\frac{\partial\psi(\mathbf{r})}{\partial x_b} \end{aligned} \tag{2.53}$$

With $\psi(\mathbf{r}) = \psi(r)$ we have

$$\begin{aligned}\langle \mathbf{r}| L_i |\psi\rangle &= -i\hbar\epsilon_{iab}x_a\frac{\partial\psi(r)}{\partial x_b} \\ &= -i\hbar\epsilon_{iab}x_a\frac{\partial r}{\partial x_b}\frac{d\psi(r)}{dr} \\ &= -i\hbar\epsilon_{iab}x_a\frac{1}{2}2x_b\frac{1}{r}\frac{d\psi(r)}{dr}\end{aligned} \tag{2.54}$$

We are left with an sum of a symmetric product $x_a x_b$ with the antisymmetric tensor ϵ_{iab} so this is zero for all $i \in [1, 3]$.

2.3.1 *Helium atom ground state energy estimation*

2.3.1.1 *Helium atom, variational method, first steps*

To verify (24.69) from [4], a six fold integral is required

$$\begin{aligned}\left\langle -\frac{\hbar^2}{2m}\left(\boldsymbol{\nabla}_1^2 + \boldsymbol{\nabla}_2^2\right)\right\rangle &= -\frac{\hbar^2}{2m}\int dr_1 d\Omega_1 r_1^2 dr_2 d\Omega_2 r_2^2 \frac{Z^6}{\pi^2 a_0^6} e^{-(r_1+r_2)Z/a_0} \\ &\quad \left(\frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial {r_1}^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2} + \frac{\partial^2}{\partial {r_2}^2}\right) e^{-(r_1+r_2)Z/a_0} \\ &= -\frac{\hbar^2}{2m}\frac{Z^6}{\pi^2 a_0^6}(4\pi)^2 \int dr_1 dr_2 r_1^2 r_2^2 e^{-(r_1+r_2)Z/a_0} \\ &\quad \left(\frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial {r_1}^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2} + \frac{\partial^2}{\partial {r_2}^2}\right) e^{-(r_1+r_2)Z/a_0}\end{aligned} \tag{2.55}$$

Making a change of variables

$$\begin{aligned}x &= \frac{Zr_1}{a_0} \\ y &= \frac{Zr_2}{a_0}\end{aligned} \tag{2.56}$$

we have

$$\begin{aligned}\left\langle -\frac{\hbar^2}{2m}\left(\boldsymbol{\nabla}_1^2+\boldsymbol{\nabla}_2^2\right)\right\rangle &= -\frac{8\hbar^2}{m}\frac{Z^2}{a_0^2}\int dxdyx^2y^2e^{-x-y}\left(\frac{2}{x}\frac{\partial}{\partial x}+\frac{\partial^2}{\partial x^2}+\frac{2}{y}\frac{\partial}{\partial y}+\frac{\partial^2}{\partial y^2}\right)e^{-x-y} \\ &= -\frac{8\hbar^2}{m}\frac{Z^2}{a_0^2}\int dxdyx^2y^2e^{-x-y}\left(-\frac{2}{x}+1-\frac{2}{y}+1\right)e^{-x-y} \\ &= \frac{16\hbar^2}{m}\frac{Z^2}{a_0^2}\int dxdyx^2y^2e^{-2x-2y}\left(\frac{1}{x}+\frac{1}{y}-1\right) \\ &= \frac{\hbar^2}{m}\frac{Z^2}{a_0^2}\end{aligned} \tag{2.57}$$

With

$$a_0 = \frac{\hbar^2}{me^2}, \tag{2.58}$$

We have the result from the text

$$\left\langle -\frac{\hbar^2}{2m}\left(\boldsymbol{\nabla}_1^2+\boldsymbol{\nabla}_2^2\right)\right\rangle = \frac{Z^2e^2}{a_0} \tag{2.59}$$

Verification of (24.70) follows in a similar fashion. We have

$$\begin{aligned}\left\langle 2e^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\right\rangle &= 2e^2\frac{Z^6}{\pi^2a_0^6}(4\pi)^2\int e^{-2(r_1+r_2)Z/a_0}r_1^2r_2^2dr_1dr_2\left(\frac{1}{r_1}+\frac{1}{r_2}\right) \\ &= 32e^2\frac{Z}{a_0}\int e^{-2x-2y}x^2y^2dxdy\left(\frac{1}{x}+\frac{1}{y}\right) \\ &= 4e^2\frac{Z}{a_0}\end{aligned} \tag{2.60}$$

2.3.1.2 *Problem with subsequent derivation*

In §24.2.1 of the text [4] is an expectation value calculation associated with the Helium atom. One of the equations (24.76) seems wrong (according to hand calculation as shown below and according to Mathematica). Is there another compensating error somewhere? Here I work the entire calculation in detail to attempt to find this.

We start with

$$\begin{aligned}\left\langle \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle &= \left(\frac{Z^3}{\pi a_0^3} \right)^2 e^2 \int d^3k d^3r_1 d^3r_2 \frac{1}{2\pi^2 k^2} e^{i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)} e^{-2Z(r_1+r_2)/a_0} \\ &= \left(\frac{Z^3}{\pi a_0^3} \right)^2 e^2 \frac{1}{2\pi^2} \int d^3k \frac{1}{k^2} \int d^3r_1 e^{i\mathbf{k}\cdot\mathbf{r}_1} e^{-2Zr_1/a_0} \int d^3r_2 e^{-i\mathbf{k}\cdot\mathbf{r}_2} e^{-2Zr_2/a_0}\end{aligned} \tag{2.61}$$

To evaluate the two last integrals, I figure the author has aligned the axis for the d^3r_1 volume elements to make the integrals easier. Specifically, for the first so that $\mathbf{k}\cdot\mathbf{r}_1 = kr_1\cos\theta$, so the integral takes the form

$$\begin{aligned}\int d^3r_1 e^{i\mathbf{k}\cdot\mathbf{r}_1} e^{-2Zr_1/a_0} &= -\int r_1^2 dr_1 d\phi d(\cos\theta) e^{ikr_1\cos\theta} e^{-2Zr_1/a_0} \\ &= -2\pi \int_{r=0}^{\infty} \int_{u=1}^{-1} r^2 dr du e^{ikru} e^{-2Zr/a_0} \\ &= -2\pi \int_{r=0}^{\infty} r^2 dr \frac{1}{ikr} \left(e^{-ikr} - e^{ikr} \right) e^{-2Zr/a_0} \\ &= \frac{4\pi}{k} \int_{r=0}^{\infty} r dr \frac{1}{2i} \left(e^{ikr} - e^{-ikr} \right) e^{-2Zr/a_0} \\ &= \frac{4\pi}{k} \int_{r=0}^{\infty} r dr \sin(kr) e^{-2Zr/a_0}\end{aligned} \tag{2.62}$$

For this last, Mathematica gives me (24.75) from the text

$$\int d^3r_1 e^{i\mathbf{k}\cdot\mathbf{r}_1} e^{-2Zr_1/a_0} = \frac{16\pi Z a_0^3}{(k^2 a_0^2 + 4Z^2)^2} \tag{2.63}$$

For the second integral, if we align the axis so that $-\mathbf{k}\cdot\mathbf{r}_2 = kr\cos\theta$ and repeat, then we have

$$\begin{aligned}\left\langle \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle &= \left(\frac{Z^3}{\pi a_0^3} \right)^2 e^2 \frac{1}{2\pi^2} 16^2 \pi^2 Z^2 a_0^6 \int d^3k \frac{1}{k^2} \frac{1}{(k^2 a_0^2 + 4Z^2)^4} \\ &= \frac{128 Z^8}{\pi^2} e^2 \int dk d\Omega \frac{1}{(k^2 a_0^2 + 4Z^2)^4} \\ &= \frac{512 Z^8}{\pi} e^2 \int dk \frac{1}{(k^2 a_0^2 + 4Z^2)^4} \\ &= \frac{512 Z^8}{\pi} e^2 \int dk \frac{1}{(k^2 a_0^2 + 4Z^2)^4}\end{aligned} \tag{2.64}$$

With $ka_0 = 2Z\kappa$ this is

$$\begin{aligned}\left\langle \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle &= \frac{512Z^8}{\pi} e^2 \int d\kappa \frac{2Z}{a_0} \frac{1}{(2Z)^8(\kappa^2+1)^4} \\ &= \frac{4Z}{\pi a_0} e^2 \int d\kappa \frac{1}{(\kappa^2+1)^4}\end{aligned} \tag{2.65}$$

Here I note that

$$\frac{d}{d\kappa} \frac{-1}{3(1+x)^3} = \frac{1}{(1+x)^4} \tag{2.66}$$

so the definite integral has the value

$$\int_0^\infty d\kappa \frac{1}{(\kappa^2+1)^4} = \frac{-1}{3(1+\infty)^3} - \frac{-1}{3(1+0)^3} = \frac{1}{3} \tag{2.67}$$

(not $5\pi/3$ as claimed in the text). This gives us

$$\begin{aligned}\left\langle \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle &= \frac{4Ze^2}{\pi a_0} \int d\kappa \frac{1}{(\kappa^2+1)^4} \\ &= \frac{4Ze^2}{3\pi a_0} \\ &\approx 0.424 \frac{Ze^2}{a_0} \neq \frac{5}{8} \frac{Ze^2}{a_0}\end{aligned} \tag{2.68}$$

So, no compensating error is found, yet the end result of the calculation, which requires the $5/8$ result matches with the results obtained other ways (as in problem set III). How would this be accounted for? Is there an error above?

2.3.2 *Curious problem using the variational method to find the ground state energy of the Harmonic oscillator*

2.3.2.1 *Recap. Variational method to find the ground state energy*

Problem 3 of §24.4 in the text [4] is an interesting one. It asks to use the variational method to find the ground state energy of a one dimensional harmonic oscillator Hamiltonian.

Somewhat unexpectedly, once I take derivatives equate to zero, I find that the variational parameter beta becomes imaginary?

I tried this twice on paper and pencil, both times getting the same thing. This seems like a noteworthy problem, and one worth reflecting on a bit.

2.3.2.2 *Recap. The variational method*

Given any, not necessarily normalized wavefunction, with a series representation specified using the energy eigenvectors for the space

$$|\psi\rangle = \sum_m c_m |\psi_m\rangle, \tag{2.69}$$

where

$$H|\psi_m\rangle = E_m |\psi_m\rangle, \tag{2.70}$$

and

$$\langle\psi_m|\psi_n\rangle = \delta_{mn}. \tag{2.71}$$

We can perform an energy expectation calculation with respect to this more general state

$$\begin{aligned}
\langle\psi| H |\psi\rangle &= \sum_m c_m^* \langle\psi_m| H \sum_n c_n |\psi_n\rangle \\
&= \sum_m c_m^* \langle\psi_m| \sum_n c_n E_n |\psi_n\rangle \\
&= \sum_{m,n} c_m^* c_n E_n \langle\psi_m|\psi_n\rangle \\
&\sum_m |c_m|^2 E_m \\
&\geq \sum_m |c_m|^2 E_0 \\
&= E_0 \langle\psi|\psi\rangle
\end{aligned} \tag{2.72}$$

This allows us to form an estimate of the ground state energy for the system, by using any state vector formed from a superposition of energy eigenstates, by simply calculating

$$E_0 \leq \frac{\langle\psi| H |\psi\rangle}{\langle\psi|\psi\rangle}. \tag{2.73}$$

One of the examples in the text is to use this to find an approximation of the ground state energy for the Helium atom Hamiltonian

$$H = -\frac{\hbar^2}{2m}\left(\boldsymbol{\nabla}_1^2 + \boldsymbol{\nabla}_1^2\right) - 2e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{2.74}$$

This calculation is performed using a trial function that was a solution of the interaction free Hamiltonian

$$\phi = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0}. \tag{2.75}$$

This is despite the fact that this is not a solution to the interaction Hamiltonian. The end result ends up being pretty close to the measured value (although there is a pesky error in the book that appears to require a compensating error somewhere else).

Part of the variational technique used in that problem, is to allow Z to vary, and then once the normalized expectation is computed, set the derivative of that equal to zero to calculate the trial wavefunction as a parameter of Z that has the lowest energy eigenstate for a function of that form. We find considering the Harmonic oscillator that this final variation does not necessarily produce meaningful results.

2.3.2.3 *The Harmonic oscillator variational problem*

The problem asks for the use of the trial wavefunction

$$\phi = e^{-\beta|x|}, \tag{2.76}$$

to perform the variational calculation above for the Harmonic oscillator Hamiltonian, which has the one dimensional position space representation

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2. \tag{2.77}$$

We can find the normalization easily

$$\begin{aligned}
\langle\phi|\phi\rangle &= \int_{-\infty}^{\infty} e^{-2\beta|x|} dx \\
&= 2\frac{1}{2\beta}\int_0^{\infty} e^{-2\beta x} 2\beta dx \\
&= 2\frac{1}{2\beta}\int_0^{\infty} e^{-u} du \\
&= \frac{1}{\beta}
\end{aligned} \tag{2.78}$$

Using integration by parts, we find for the energy expectation

$$\begin{aligned}\langle\phi|\, H\,|\phi\rangle &= \int_{-\infty}^{\infty} dx e^{-\beta|x|}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}m\omega^2x^2\right)e^{-\beta|x|} \\ &= \lim_{\epsilon\to 0}\left(\int_{-\infty}^{-\epsilon}+\int_{-\epsilon}^{\epsilon}+\int_{\epsilon}^{\infty}\right)dx e^{-\beta|x|}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}m\omega^2x^2\right)e^{-\beta|x|} \\ &= 2\int_0^{\infty} dx e^{-2\beta x}\left(-\frac{\hbar^2\beta^2}{2m}+\frac{1}{2}m\omega^2x^2\right)-\frac{\hbar^2}{2m}\lim_{\epsilon\to 0}\int_{-\epsilon}^{\epsilon}dx e^{-\beta|x|}\frac{d^2}{dx^2}e^{-\beta|x|}\end{aligned} \tag{2.79}$$

The first integral we can do

$$\begin{aligned}2\int_0^{\infty} dx e^{-2\beta x}\left(-\frac{\hbar^2\beta^2}{2m}+\frac{1}{2}m\omega^2x^2\right) &= -\frac{\hbar^2\beta^2}{m}\int_0^{\infty}dx e^{-2\beta x}+m\omega^2\int_0^{\infty}dx x^2e^{-2\beta x} \\ &= -\frac{\hbar^2\beta}{2m}\int_0^{\infty}du e^{-u}+\frac{m\omega^2}{8\beta^3}\int_0^{\infty}du u^2e^{-u} \\ &= -\frac{\beta\hbar^2}{2m}+\frac{m\omega^2}{4\beta^3}\end{aligned} \tag{2.80}$$

A naive evaluation of this integral requires the origin to be avoided where the derivative of $|x|$ becomes undefined. This also provides a nice way to evaluate this integral because we can double the integral and half the range, eliminating the absolute value.

However, can we assume that the remaining integral is zero?

I thought that we could, but the end result is curious. I also verified my calculation symbolically in 24.4.3_attempt_with_mathematica.nb , but found that Mathematica required some special hand holding to deal with the origin. Initially I coded this by avoiding the origin as above, but later switched to $|x| = \sqrt{x^2}$ which Mathematica treats more gracefully.

Without that last integral, involving our singular $|x|'$ and $|x|''$ terms, our ground state energy estimation, parameterized by β is

$$E[\beta] = -\frac{\beta^2\hbar^2}{2m}+\frac{m\omega^2}{4\beta^2}. \tag{2.81}$$

Observe that if we set the derivative of this equal to zero to find the "best" beta associated with this trial function

$$0 = \frac{\partial E}{\partial\beta} = -\frac{\beta\hbar^2}{2m}-\frac{m\omega^2}{2\beta^3} \tag{2.82}$$

we find that the parameter beta that best minimizes this ground state energy function is complex with value

$$\beta^2 = \pm \frac{im\omega}{\sqrt{2}\,\hbar}. \tag{2.83}$$

It appears at first glance that we can not minimize eq. (2.81) to find a best ground state energy estimate associated with the trial function eq. (2.76). We do however, know the exact ground state energy $\hbar\omega/2$ for the Harmonic oscillator. Is is possible to show that for all β^2 we have

$$\frac{\hbar\omega}{2} \leq -\frac{\beta^2\hbar^2}{2m} + \frac{m\omega^2}{4\beta^2} \tag{2.84}$$

? This inequality would be expected if we can assume that the trial wavefunction has a Fourier series representation utilizing the actual energy eigenfunctions for the system.

The resolution to this question is avoided once we include the singularity. This is explored in the last part of these notes.

2.3.2.4 *Is our trial function representable?*

I thought perhaps that since the trial wave function for this problem lies outside the span of the Hilbert space that describes the solutions to the Harmonic oscillator. Another thing of possible interest is the trouble near the origin for this wave function, when operated on by $P^2/2m$, and this has been (incorrectly assumed to have zero contribution above).

I had initially thought that part of the value of this variational method was that we can use it despite not even knowing what the exact solution is (and in the case of the Helium atom, I believe it was stated in class that an exact closed form solution is not even known). This makes me wonder what restrictions must be imposed on the trial solutions to get a meaningful answer from the variational calculation?

Suppose that the trial wavefunction is not representable in the solution space. If that is the case, we need to adjust the treatment to account for that. Suppose we have

$$|\phi\rangle = \sum_n c_n |\psi_n\rangle + c_\perp |\psi_\perp\rangle\,. \tag{2.85}$$

where $|\psi_\perp\rangle$ is unknown, and presumed not orthogonal to any of the energy eigenkets. We can still calculate the norm of the trial function

$$\begin{aligned}\langle\phi|\phi\rangle &= \sum_{n,m}\langle c_n\psi_n + c_\perp\psi_\perp|c_m\psi_m + c_\perp\psi_\perp\rangle \\ &= \sum_n |c_n|^2 + c_n^* c_\perp\langle\psi_n|\psi_\perp\rangle + c_n c_\perp^*\langle\psi_\perp|\psi_n\rangle + |c_\perp|^2\langle\psi_\perp|\psi_\perp\rangle \\ &= \langle\psi_\perp|\psi_\perp\rangle + \sum_n |c_n|^2 + 2\,\mathrm{Re}\left(c_n^* c_\perp\langle\psi_n|\psi_\perp\rangle\right).\end{aligned} \tag{2.86}$$

Similarly we can calculate the energy expectation for this unnormalized state and find

$$\begin{aligned}\langle\phi|H|\phi\rangle &= \sum_{n,m}\langle c_n\psi_n + c_\perp\psi_\perp|H|c_m\psi_m + c_\perp\psi_\perp\rangle \\ &= \sum_n |c_n|^2 E_n + c_n^* c_\perp E_n\langle\psi_n|\psi_\perp\rangle + c_n c_\perp^* E_n\langle\psi_\perp|\psi_n\rangle + |c_\perp|^2\langle\psi_\perp|H|\psi_\perp\rangle\end{aligned} \tag{2.87}$$

Our normalized energy expectation is therefore the considerably messier

$$\begin{aligned}\frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle} &= \frac{\sum_n |c_n|^2 E_n + c_n^* c_\perp E_n\langle\psi_n|\psi_\perp\rangle + c_n c_\perp^* E_n\langle\psi_\perp|\psi_n\rangle + |c_\perp|^2\langle\psi_\perp|H|\psi_\perp\rangle}{\langle\psi_\perp|\psi_\perp\rangle + \sum_m |c_m|^2 + 2\,\mathrm{Re}\left(c_m^* c_\perp\langle\psi_m|\psi_\perp\rangle\right)} \\ &\geq \frac{\sum_n |c_n|^2 E_0 + c_n^* c_\perp E_n\langle\psi_n|\psi_\perp\rangle + c_n c_\perp^* E_n\langle\psi_\perp|\psi_n\rangle + |c_\perp|^2\langle\psi_\perp|H|\psi_\perp\rangle}{\langle\psi_\perp|\psi_\perp\rangle + \sum_m |c_m|^2 + 2\,\mathrm{Re}\left(c_m^* c_\perp\langle\psi_m|\psi_\perp\rangle\right)}\end{aligned} \tag{2.88}$$

With a requirement to include the perpendicular cross terms the norm does not just cancel out, leaving us with a clean estimation of the ground state energy. In order to utilize this variational method, we implicitly have an assumption that the $\langle\psi_\perp|\psi_\perp\rangle$ and $\langle\psi_m|\psi_\perp\rangle$ terms in the denominator are sufficiently small that they can be neglected.

2.3.2.5 *Calculating the Fourier terms*

In order to see how much a problem representing this trial function in the Harmonic oscillator wavefunction solution space, we can just calculate the Fourier fit.

Our first few basis functions, with $\alpha = \sqrt{m\omega/\hbar}$ are

$$\begin{aligned}u_0 &= \sqrt{\frac{\alpha}{\sqrt{\pi}}}e^{-\alpha^2x^2/2} \\ u_1 &= \sqrt{\frac{\alpha}{2\sqrt{\pi}}}(2\alpha x)e^{-\alpha^2x^2/2} \\ u_2 &= \sqrt{\frac{\alpha}{8\sqrt{\pi}}}(4\alpha^2x^2 - 2)e^{-\alpha^2x^2/2}\end{aligned} \tag{2.89}$$

In general our wavefunctions are

$$\begin{aligned} u_n &= N_n H_n(\alpha x) e^{-\alpha^2 x^2/2} \\ N_n &= \sqrt{\frac{\alpha}{\sqrt{\pi} 2^n n!}} \\ H_n(\eta) &= (-1)^n e^{\eta^2} \frac{d^n}{d\eta^n} e^{-\eta^2} \end{aligned} \tag{2.90}$$

From which we find

$$\psi(x) = e^{-\alpha^2 x^2/2} (N_n)^2 H_n(\alpha x) \int_{-\infty}^{\infty} H_n(\alpha x) e^{-\alpha^2 x^2/2} \psi(x) dx \tag{2.91}$$

Our wave function, with $\beta = 1$ is plotted in fig. 2.3

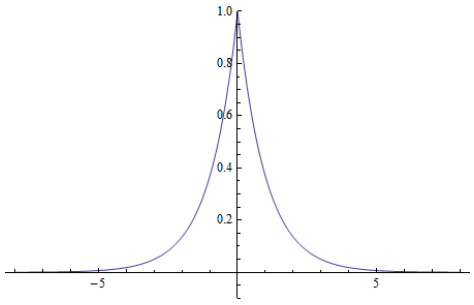

Figure 2.3: Exponential trial function with absolute exponential die off

The zeroth order fitting using the Gaussian exponential is found to be

$$\psi_0(x) = \sqrt{2\beta}\,\mathrm{erfc}\left(\frac{\beta}{\sqrt{2}\alpha}\right) e^{-\alpha^2 x^2/2 + \beta^2/(2\alpha^2)} \tag{2.92}$$

With $\alpha = \beta = 1$, this is plotted in fig. 2.4 and can be seen to match fairly well

The higher order terms get small fast, but we can see in fig. 2.5, where a tenth order fitting is depicted that it would take a number of them to get anything close to the sharp peak that we have in our exponential trial function.

Note that all the brakets of even orders in n with the trial function are zero, which is why the tenth order approximation is only a sum of six terms.

Details for this harmonic oscillator wavefunction fitting can be found in gaussian_fitting_for_abs_function.nb can be found separately, calculated using a Mathematica worksheet.

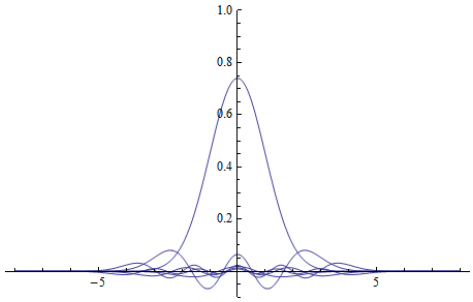

Figure 2.4: First ten orders, fitting harmonic oscillator wavefunctions to this trial function

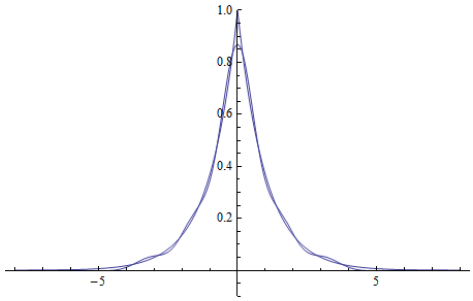

Figure 2.5: Tenth order harmonic oscillator wavefunction fitting

The question of interest is why we can approximate the trial function so nicely (except at the origin) even with just a first order approximation (polynomial times Gaussian functions where the polynomials are Hankel functions), and we can get an exact value for the lowest energy state using the first order approximation of our trial function, why do we get garbage from the variational method, where enough terms are implicitly included that the peak should be sharp. It must therefore be important to consider the origin, but how do we give some meaning to the derivative of the absolute value function? The key (supplied when asking Professor Sipe in office hours for the course) is to express the absolute value function in terms of Heavyside step functions, for which the derivative can be identified as the delta function.

2.3.2.6 *Correcting, treating the origin this way*

Here is how we can express the absolute value function using the Heavyside step

$$|x| = x\theta(x) - x\theta(-x), \tag{2.93}$$

where the step function is zero for $x < 0$ and one for $x > 0$ as plotted in fig. 2.6.

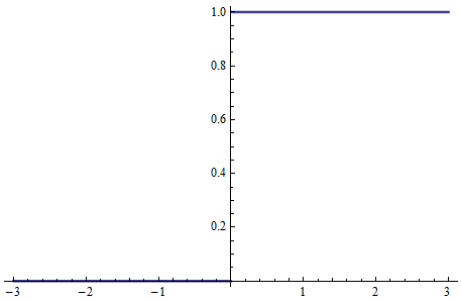

Figure 2.6: stepFunction

Expressed this way, with the identification $\theta'(x) = \delta(x)$, we have for the derivative of the absolute value function

$$\begin{aligned} |x|' &= x'\theta(x) - x'\theta(-x) + x\theta'(x) - x\theta'(-x) \\ &= \theta(x) - \theta(-x) + x\delta(x) + x\delta(-x) \\ &= \theta(x) - \theta(-x) + x\delta(x) + x\delta(x) \end{aligned} \tag{2.94}$$

Observe that we have our expected unit derivative for $x > 0$, and -1 derivative for $x < 0$. At the origin our θ contributions vanish, and we are left with

$$|x|'\Big|_{x=0} = 2\,x\delta(x)|_{x=0} \tag{2.95}$$

We have got zero times infinity here, so how do we give meaning to this? As with any delta functional, we have got to apply it to a well behaved (square integrable) test function $f(x)$ and integrate. Doing so we have

$$\begin{aligned} \int_{-\infty}^{\infty} dx|x|'f(x) &= 2\int_{-\infty}^{\infty} dx x\delta(x)f(x) \\ &= 2(0)f(0) \end{aligned} \tag{2.96}$$

This equals zero for any well behaved test function $f(x)$. Since the delta function only picks up the contribution at the origin, we can therefore identify $|x|'$ as zero at the origin.

Using the same technique, we can express our trial function in terms of steps

$$\psi = e^{-\beta|x|} = \theta(x)e^{-\beta x} + \theta(-x)e^{\beta x}. \tag{2.97}$$

This we can now take derivatives of, even at the origin, and find

$$\begin{aligned}\psi' &= \theta'(x)e^{-\beta x} + \theta'(-x)e^{\beta x} - \beta\theta(x)e^{-\beta x} + \beta\theta(-x)e^{\beta x} \\ &= \delta(x)e^{-\beta x} - \delta(-x)e^{\beta x} - \beta\theta(x)e^{-\beta x} + \beta\theta(-x)e^{\beta x} \\ &= \cancel{\delta(x)e^{-\beta x} = \delta(x)e^{\beta x}} - \beta\theta(x)e^{-\beta x} + \beta\theta(-x)e^{\beta x} \\ &= \beta\left(-\theta(x)e^{-\beta x} + \theta(-x)e^{\beta x}\right)\end{aligned} \tag{2.98}$$

Taking second derivatives we find

$$\begin{aligned}\psi'' &= \beta\left(-\theta'(x)e^{-\beta x} + \theta'(-x)e^{\beta x} + \beta\theta(x)e^{-\beta x} + \beta\theta(-x)e^{\beta x}\right) \\ &= \beta\left(-\delta(x)e^{-\beta x} - \delta(-x)e^{\beta x} + \beta\theta(x)e^{-\beta x} + \beta\theta(-x)e^{\beta x}\right) \\ &= \beta^2\psi - 2\beta\delta(x)\end{aligned} \tag{2.99}$$

Now application of the Hamiltonian operator on our trial function gives us

$$H\psi = -\frac{\hbar^2}{2m}\left(\beta^2\psi - 2\delta(x)\right) + \frac{1}{2}m\omega^2x^2\psi, \tag{2.100}$$

so

$$\begin{aligned}\langle\psi|\,H\,|\psi\rangle &= \int_{-\infty}^{\infty}\left(-\frac{\hbar^2\beta^2}{2m} + \frac{1}{2}m\omega^2x^2\right)e^{-2\beta|x|} + \frac{\hbar^2\beta}{m}\int_{-\infty}^{\infty}\delta(x)e^{-\beta|x|} \\ &= -\frac{\beta\hbar^2}{2m} + \frac{m\omega^2}{4\beta^3} + \frac{\hbar^2\beta}{m} \\ &= \frac{\beta\hbar^2}{2m} + \frac{m\omega^2}{4\beta^3}.\end{aligned} \tag{2.101}$$

Normalized we have

$$E[\beta] = \frac{\langle\psi|\,H\,|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\beta^2\hbar^2}{2m} + \frac{m\omega^2}{4\beta^2}. \tag{2.102}$$

This is looking much more promising. We will have the sign alternation that we require to find a positive, non-complex, value for β when $E[\beta]$ is minimized. That is

$$0 = \frac{\partial E}{\partial\beta} = \frac{\beta\hbar^2}{m} - \frac{m\omega^2}{2\beta^3}, \tag{2.103}$$

so the extremum is found at

$$\beta^4 = \frac{m^2\omega^2}{2\hbar^2}. \tag{2.104}$$

Plugging this back in we find that our trial function associated with the minimum energy (unnormalized still) is

$$\psi = e^{-\sqrt{\frac{m\omega x^2}{\sqrt{2}\hbar}}}, \tag{2.105}$$

and that energy, after substitution, is

$$E[\beta_{\text{min}}] = \frac{\hbar\omega}{2}\sqrt{2} \tag{2.106}$$

We have something that is 1.4× the true ground state energy, but is at least a ball park value. However, to get this result, we have to be very careful to treat our point of singularity. A derivative that we would call undefined in first year calculus, is not only defined, but required, for this treatment to work!

3

TIME INDEPENDENT PERTURBATION THEORY

See §16.1 of the text [4].

We can sometimes use this sort of physical insight to help construct a good approximation. This is provided that we have some of this physical insight, or that it is good insight in the first place.

This is the no-think (turn the crank) approach.

Here we split our Hamiltonian into two parts

$$H = H_0 + H' \tag{3.1}$$

where H_0 is a Hamiltonian for which we know the energy eigenstates and the eigenkets. The H' is the "perturbation" that is supposed to be small "in some sense".

Prof Sipe will provide some references later that provide a more specific meaning to this "smallness". From some ad-hoc discussion in the class it sounds like one has to consider sequences of operators, and look at the convergence of those sequences (is this L2 measure theory?)

We would like to consider a range of problems of the form

$$H = H_0 + \lambda H' \tag{3.2}$$

where

$$\lambda \in [0, 1] \tag{3.3}$$

So that when $\lambda \to 0$ we have

$$H \to H_0 \tag{3.4}$$

the problem that we already know, but for $\lambda \to 1$ we have

$$H = H_0 + H' \tag{3.5}$$

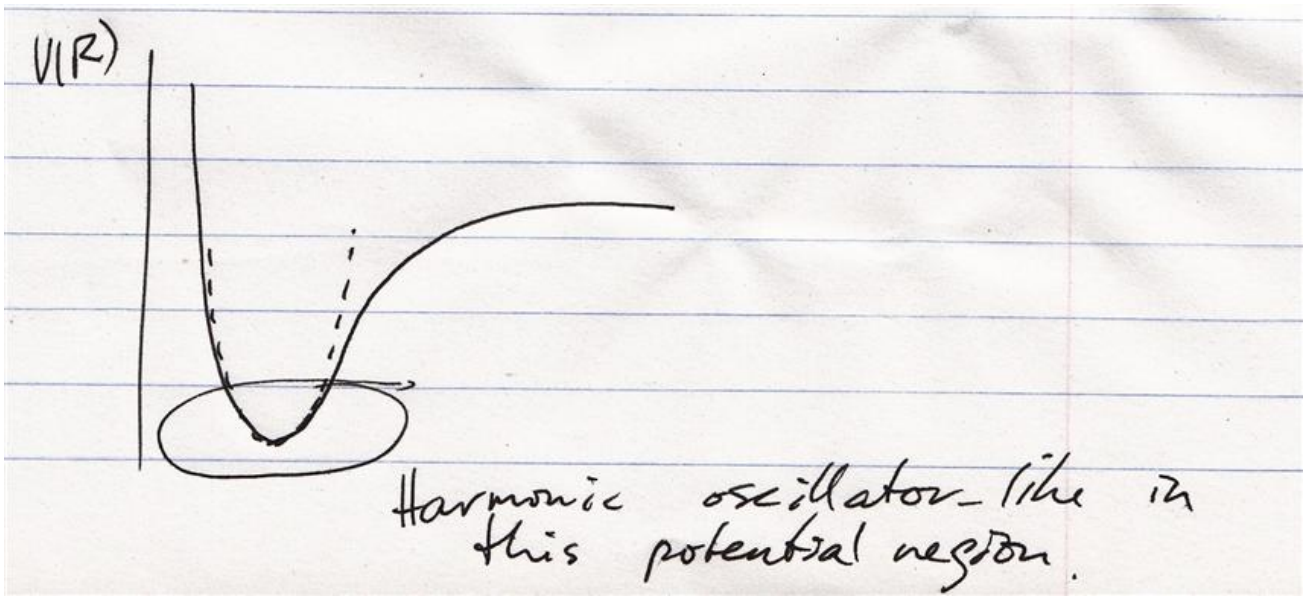

Figure 3.1: Example of small perturbation from known Hamiltonian

the problem that we would like to solve.

We are assuming that we know the eigenstates and eigenvalues for H_0. Assuming no degeneracy

$$H_0 \left|\psi_s^{(0)}\right\rangle = E_s^{(0)} \left|\psi_s^{(0)}\right\rangle \tag{3.6}$$

We seek

$$(H_0 + H') \left|\psi_s\right\rangle = E_s \left|\psi_s\right\rangle \tag{3.7}$$

(this is the $\lambda = 1$ case).

Once (if) found, when $\lambda \to 0$ we will have

$$\begin{aligned} E_s &\to E_s^{(0)} \\ \left|\psi_s\right\rangle &\to \left|\psi_s^{(0)}\right\rangle \end{aligned} \tag{3.8}$$

$$E_s = E_s^{(0)} + \lambda E_s^{(1)} + \lambda^2 E_s^{(2)} \tag{3.9}$$

$$\psi_s = \sum_n c_{ns} \left|\psi_n^{(0)}\right\rangle \tag{3.10}$$

This we know we can do because we are assumed to have a complete set of states.
with

$$c_{ns} = c_{ns}^{(0)} + \lambda c_{ns}^{(1)} + \lambda^2 c_{ns}^{(2)} \tag{3.11}$$

where

$$c_{ns}^{(0)} = \delta_{ns} \tag{3.12}$$

There is a subtlety here that will be treated differently from the text. We write

$$\begin{aligned} |\psi_s\rangle &= \left|\psi_s^{(0)}\right\rangle + \lambda \sum_n c_{ns}^{(1)} \left|\psi_n^{(0)}\right\rangle + \lambda^2 \sum_n c_{ns}^{(2)} \left|\psi_n^{(0)}\right\rangle + \cdots \\ &= \left(1 + \lambda c_{ss}^{(1)} + \cdots\right) \left|\psi_s^{(0)}\right\rangle + \lambda \sum_{n \neq s} c_{ns}^{(1)} \left|\psi_n^{(0)}\right\rangle + \cdots \end{aligned} \tag{3.13}$$

Take

$$\begin{aligned} \left|\bar{\psi}_s\right\rangle &= \left|\bar{\psi}_s^{(0)}\right\rangle + \lambda \frac{\sum_{n \neq s} c_{ns}^{(1)} \left|\psi_n^{(0)}\right\rangle}{1 + \lambda c_{ss}^{(1)}} + \cdots \\ &= \left|\bar{\psi}_s^{(0)}\right\rangle + \lambda \sum_{n \neq s} \bar{c}_{ns}^{(1)} \left|\psi_n^{(0)}\right\rangle + \cdots \end{aligned} \tag{3.14}$$

where

$$\bar{c}_{ns}^{(1)} = \frac{c_{ns}^{(1)}}{1 + \lambda c_{ss}^{(1)}} \tag{3.15}$$

We have:

$$\begin{aligned} \bar{c}_{ns}^{(1)} &= c_{ns}^{(1)} \\ \bar{c}_{ns}^{(2)} &\neq c_{ns}^{(2)} \end{aligned} \tag{3.16}$$

FIXME: I missed something here.
Note that this is no longer normalized.

$$\left\langle \bar{\psi}_s \middle| \bar{\psi}_s \right\rangle \neq 1 \tag{3.17}$$

3.1 TIME INDEPENDENT PERTURBATION

The setup To recap, we were covering the time independent perturbation methods from §16.1 of the text [4]. We start with a known Hamiltonian H_0, and alter it with the addition of a "small" perturbation

$$H = H_0 + \lambda H', \qquad \lambda \in [0, 1] \tag{3.18}$$

For the original operator, we assume that a complete set of eigenvectors and eigenkets is known

$$H_0 \left|\psi_s{}^{(0)}\right\rangle = E_s{}^{(0)} \left|\psi_s{}^{(0)}\right\rangle \tag{3.19}$$

We seek the perturbed eigensolution

$$H \left|\psi_s\right\rangle = E_s \left|\psi_s\right\rangle \tag{3.20}$$

and assumed a perturbative series representation for the energy eigenvalues in the new system

$$E_s = E_s{}^{(0)} + \lambda E_s{}^{(1)} + \lambda^2 E_s{}^{(2)} + \cdots \tag{3.21}$$

Given an assumed representation for the new eigenkets in terms of the known basis

$$\left|\psi_s\right\rangle = \sum_n c_{ns} \left|\psi_n{}^{(0)}\right\rangle \tag{3.22}$$

and a pertubative series representation for the probability coefficients

$$c_{ns} = c_{ns}{}^{(0)} + \lambda c_{ns}{}^{(1)} + \lambda^2 c_{ns}{}^{(2)}, \tag{3.23}$$

so that

$$\left|\psi_s\right\rangle = \sum_n c_{ns}{}^{(0)} \left|\psi_n{}^{(0)}\right\rangle + \lambda \sum_n c_{ns}{}^{(1)} \left|\psi_n{}^{(0)}\right\rangle + \lambda^2 \sum_n c_{ns}{}^{(2)} \left|\psi_n{}^{(0)}\right\rangle + \cdots \tag{3.24}$$

Setting $\lambda = 0$ requires

$$c_{ns}{}^{(0)} = \delta_{ns}, \tag{3.25}$$

for

$$\begin{aligned}|\psi_s\rangle &= \left|\psi_s{}^{(0)}\right\rangle + \lambda \sum_n c_{ns}{}^{(1)} \left|\psi_n{}^{(0)}\right\rangle + \lambda^2 \sum_n c_{ns}{}^{(2)} \left|\psi_n{}^{(0)}\right\rangle + \cdots \\ &= \left(1 + \lambda c_{ss}{}^{(1)} + \lambda^2 c_{ss}{}^{(2)} + \cdots\right)\left|\psi_s{}^{(0)}\right\rangle + \lambda \sum_{n\neq s} c_{ns}{}^{(1)} \left|\psi_n{}^{(0)}\right\rangle + \lambda^2 \sum_{n\neq s} c_{ns}{}^{(2)} \left|\psi_n{}^{(0)}\right\rangle + \cdots\end{aligned} \tag{3.26}$$

We rescaled our kets

$$\left|\bar{\psi}_s\right\rangle = \left|\psi_s{}^{(0)}\right\rangle + \lambda \sum_{n\neq s} \bar{c}_{ns}{}^{(1)} \left|\psi_n{}^{(0)}\right\rangle + \lambda^2 \sum_{n\neq s} \bar{c}_{ns}{}^{(2)} \left|\psi_n{}^{(0)}\right\rangle + \cdots \tag{3.27}$$

where

$$\bar{c}_{ns}{}^{(j)} = \frac{c_{ns}{}^{(j)}}{1 + \lambda c_{ss}{}^{(1)} + \lambda^2 c_{ss}{}^{(2)} + \cdots} \tag{3.28}$$

The normalization of the rescaled kets is then

$$\left\langle\bar{\psi}_s\middle|\bar{\psi}_s\right\rangle = 1 + \lambda^2 \sum_{n\neq s} \left|\bar{c}_{ss}{}^{(1)}\right|^2 + \cdots \equiv \frac{1}{Z_s}, \tag{3.29}$$

One can then construct a renormalized ket if desired

$$\left|\bar{\psi}_s\right\rangle_R = Z_s^{1/2} \left|\bar{\psi}_s\right\rangle, \tag{3.30}$$

so that

$$\left(\left|\bar{\psi}_s\right\rangle_R\right)^\dagger \left|\bar{\psi}_s\right\rangle_R = Z_s \left\langle\bar{\psi}_s\middle|\bar{\psi}_s\right\rangle = 1. \tag{3.31}$$

The meat That is as far as we got last time. We continue by renaming terms in eq. (3.27)

$$\left|\bar{\psi}_s\right\rangle = \left|\psi_s{}^{(0)}\right\rangle + \lambda \left|\psi_s{}^{(1)}\right\rangle + \lambda^2 \left|\psi_s{}^{(2)}\right\rangle + \cdots \tag{3.32}$$

where

$$\left|\psi_s{}^{(j)}\right\rangle = \sum_{n\neq s} \bar{c}_{ns}{}^{(j)} \left|\psi_n{}^{(0)}\right\rangle. \tag{3.33}$$

Now we act on this with the Hamiltonian

$$H\left|\bar{\psi}_s\right\rangle = E_s\left|\bar{\psi}_s\right\rangle, \tag{3.34}$$

or

$$H\left|\bar{\psi}_s\right\rangle - E_s\left|\bar{\psi}_s\right\rangle = 0. \tag{3.35}$$

Expanding this, we have

$$\begin{aligned}&(H_0+\lambda H')\left(\left|{\psi_s}^{(0)}\right\rangle + \lambda\left|{\psi_s}^{(1)}\right\rangle + \lambda^2\left|{\psi_s}^{(2)}\right\rangle + \cdots\right)\\ &\quad -\left({E_s}^{(0)} + \lambda {E_s}^{(1)} + \lambda^2 {E_s}^{(2)} + \cdots\right)\left(\left|{\psi_s}^{(0)}\right\rangle + \lambda\left|{\psi_s}^{(1)}\right\rangle + \lambda^2\left|{\psi_s}^{(2)}\right\rangle + \cdots\right) = 0.\end{aligned} \tag{3.36}$$

We want to write this as

$$|A\rangle + \lambda|B\rangle + \lambda^2|C\rangle + \cdots = 0. \tag{3.37}$$

This is

$$\begin{aligned}0 &= \lambda^0(H_0 - E_s^{(0)})\left|{\psi_s}^{(0)}\right\rangle\\ &\quad + \lambda\left((H_0 - E_s^{(0)})\left|{\psi_s}^{(1)}\right\rangle + (H' - E_s^{(1)})\left|{\psi_s}^{(0)}\right\rangle\right)\\ &\quad + \lambda^2\left((H_0 - E_s^{(0)})\left|{\psi_s}^{(2)}\right\rangle + (H' - E_s^{(1)})\left|{\psi_s}^{(1)}\right\rangle - E_s^{(2)}\left|{\psi_s}^{(0)}\right\rangle\right)\\ &\quad \cdots\end{aligned} \tag{3.38}$$

So we form

$$\begin{aligned}|A\rangle &= (H_0 - E_s^{(0)})\left|{\psi_s}^{(0)}\right\rangle\\ |B\rangle &= (H_0 - E_s^{(0)})\left|{\psi_s}^{(1)}\right\rangle + (H' - E_s^{(1)})\left|{\psi_s}^{(0)}\right\rangle\\ |C\rangle &= (H_0 - E_s^{(0)})\left|{\psi_s}^{(2)}\right\rangle + (H' - E_s^{(1)})\left|{\psi_s}^{(1)}\right\rangle - E_s^{(2)}\left|{\psi_s}^{(0)}\right\rangle,\end{aligned} \tag{3.39}$$

and so forth.

Zeroth order in λ Since $H_0\left|{\psi_s}^{(0)}\right\rangle = E_s^{(0)}\left|{\psi_s}^{(0)}\right\rangle$, this first condition on $|A\rangle$ is not much more than a statement that $0 - 0 = 0$.

First order in λ How about $|B\rangle = 0$? For this to be zero we require that both of the following are simultaneously zero

$$\begin{aligned}\left\langle {\psi_s}^{(0)} \middle| B \right\rangle &= 0 \\ \left\langle {\psi_m}^{(0)} \middle| B \right\rangle &= 0, \qquad m \neq s\end{aligned} \tag{3.40}$$

This first condition is

$$\left\langle {\psi_s}^{(0)} \right| (H' - E_s^{(1)}) \left| {\psi_s}^{(0)} \right\rangle = 0. \tag{3.41}$$

With

$$\left\langle {\psi_m}^{(0)} \right| H' \left| {\psi_s}^{(0)} \right\rangle \equiv {H'}_{ms}, \tag{3.42}$$

or

$${H'}_{ss} = E_s^{(1)}. \tag{3.43}$$

From the second condition we have

$$0 = \left\langle {\psi_m}^{(0)} \right| (H_0 - E_s^{(0)}) \left| {\psi_s}^{(1)} \right\rangle + \left\langle {\psi_m}^{(0)} \right| (H' - E_s^{(1)}) \left| {\psi_s}^{(0)} \right\rangle \tag{3.44}$$

Utilizing the Hermitian nature of H_0 we can act backwards on $\left\langle {\psi_m}^{(0)} \right|$

$$\left\langle {\psi_m}^{(0)} \right| H_0 = E_m^{(0)} \left\langle {\psi_m}^{(0)} \right|. \tag{3.45}$$

We note that $\left\langle {\psi_m}^{(0)} \middle| {\psi_s}^{(0)} \right\rangle = 0, m \neq s$. We can also expand the $\left\langle {\psi_m}^{(0)} \middle| {\psi_s}^{(1)} \right\rangle$, which is

$$\left\langle {\psi_m}^{(0)} \middle| {\psi_s}^{(1)} \right\rangle = \left\langle {\psi_m}^{(0)} \right| \left(\sum_{n \neq s} {\bar{c}_{ns}}^{(1)} \left| {\psi_n}^{(0)} \right\rangle \right) \tag{3.46}$$

I found that reducing this sum was not obvious until some actual integers were plugged in. Suppose that $s = 3$, and $m = 5$, then this is

$$\begin{aligned}\left\langle {\psi_5}^{(0)} \middle| {\psi_3}^{(1)} \right\rangle &= \left\langle {\psi_5}^{(0)} \right| \left(\sum_{n=0,1,2,4,5,\cdots} {\bar{c}_{n3}}^{(1)} \left| {\psi_n}^{(0)} \right\rangle \right) \\ &= {\bar{c}_{53}}^{(1)} \left\langle {\psi_5}^{(0)} \middle| {\psi_5}^{(0)} \right\rangle \\ &= {\bar{c}_{53}}^{(1)}.\end{aligned} \tag{3.47}$$

Observe that we can also replace the superscript (1) with (j) in the above manipulation without impacting anything else. That and putting back in the abstract indices, we have the general result

$$\left\langle \psi_m{}^{(0)} \middle| \psi_s{}^{(j)} \right\rangle = \bar{c}_{ms}{}^{(j)}. \tag{3.48}$$

Utilizing this gives us

$$0 = (E_m^{(0)} - E_s^{(0)})\bar{c}_{ms}{}^{(1)} + H'_{ms} \tag{3.49}$$

And summarizing what we learn from our $|B\rangle = 0$ conditions we have

$$\begin{aligned} E_s^{(1)} &= H'_{ss} \\ \bar{c}_{ms}{}^{(1)} &= \frac{H'_{ms}}{E_s^{(0)} - E_m^{(0)}} \end{aligned} \tag{3.50}$$

Second order in λ Doing the same thing for $|C\rangle = 0$ we form (or assume)

$$\left\langle \psi_s{}^{(0)} \middle| C \right\rangle = 0 \tag{3.51}$$

$$\begin{aligned} 0 &= \left\langle \psi_s{}^{(0)} \middle| C \right\rangle \\ &= \left\langle \psi_s{}^{(0)} \middle| \left((H_0 - E_s^{(0)}) \left| \psi_s{}^{(2)} \right\rangle + (H' - E_s^{(1)}) \left| \psi_s{}^{(1)} \right\rangle - E_s^{(2)} \left| \psi_s{}^{(0)} \right\rangle \right) \right. \\ &= (E_s^{(0)} - E_s^{(0)}) \left\langle \psi_s{}^{(0)} \middle| \psi_s{}^{(2)} \right\rangle + \left\langle \psi_s{}^{(0)} \middle| (H' - E_s^{(1)}) \left| \psi_s{}^{(1)} \right\rangle - E_s^{(2)} \left\langle \psi_s{}^{(0)} \middle| \psi_s{}^{(0)} \right\rangle \end{aligned} \tag{3.52}$$

We need to know what the $\left\langle \psi_s{}^{(0)} \middle| \psi_s{}^{(1)} \right\rangle$ is, and find that it is zero

$$\left\langle \psi_s{}^{(0)} \middle| \psi_s{}^{(1)} \right\rangle = \left\langle \psi_s{}^{(0)} \right| \sum_{n \neq s} \bar{c}_{ns}{}^{(1)} \left| \psi_n{}^{(0)} \right\rangle \tag{3.53}$$

Again, suppose that $s = 3$. Our sum ranges over all $n \neq 3$, so all the brakets are zero. Utilizing that we have

$$\begin{aligned} E_s^{(2)} &= \left\langle \psi_s{}^{(0)} \right| H' \left| \psi_s{}^{(1)} \right\rangle \\ &= \left\langle \psi_s{}^{(0)} \right| H' \sum_{m \neq s} \bar{c}_{ms}{}^{(1)} \left| \psi_m{}^{(0)} \right\rangle \\ &= \sum_{m \neq s} \bar{c}_{ms}{}^{(1)} H'_{sm} \end{aligned} \tag{3.54}$$

From eq. (3.50) we have

$$E_s^{(2)} = \sum_{m\neq s} \frac{H'_{ms}}{E_s^{(0)} - E_m^{(0)}} H'_{sm} = \sum_{m\neq s} \frac{|H'_{ms}|^2}{E_s^{(0)} - E_m^{(0)}} \tag{3.55}$$

We can now summarize by forming the first order terms of the perturbed energy and the corresponding kets

$$\begin{aligned} E_s &= E_s^{(0)} + \lambda H'_{ss} + \lambda^2 \sum_{m\neq s} \frac{|H'_{ms}|^2}{E_s^{(0)} - E_m^{(0)}} + \cdots \\ \left|\bar{\psi}_s\right\rangle &= \left|\psi_s{}^{(0)}\right\rangle + \lambda \sum_{m\neq s} \frac{H'_{ms}}{E_s^{(0)} - E_m^{(0)}} \left|\psi_m{}^{(0)}\right\rangle + \cdots \end{aligned} \tag{3.56}$$

We can continue calculating, but are hopeful that we can stop the calculation without doing more work, even if $\lambda = 1$. If one supposes that the

$$\sum_{m\neq s} \frac{H'_{ms}}{E_s^{(0)} - E_m^{(0)}} \tag{3.57}$$

term is "small", then we can hope that truncating the sum will be reasonable for $\lambda = 1$. This would be the case if

$$H'_{ms} \ll \left|E_s^{(0)} - E_m^{(0)}\right|, \tag{3.58}$$

however, to put some mathematical rigor into making a statement of such smallness takes a lot of work. We are referred to [10]. Incidentally, these are loosely referred to as the first and second testaments, because of the author's name, and the fact that they came as two volumes historically.

3.2 ISSUES CONCERNING DEGENERACY

When the perturbed state is non-degenerate Suppose the state of interest is non-degenerate but others are

FIXME: diagram. states designated by dashes labeled $n1$, $n2$, $n3$ degeneracy $\alpha = 3$ for energy $E_n^{(0)}$.

This is no problem except for notation, and if the analysis is repeated we find

$$E_s = E_s^{(0)} + \lambda H'_{ss} + \lambda^2 \sum_{m\neq s,\alpha} \frac{\left|H'_{m\alpha;s}\right|^2}{E_s^{(0)} - E_m^{(0)}} + \cdots \tag{3.59}$$

$$\left|\bar{\psi}_s\right\rangle = \left|{\psi_s}^{(0)}\right\rangle + \lambda \sum_{m\neq s,\alpha} \frac{H'_{m\alpha;s}}{E_s^{(0)} - E_m^{(0)}} \left|{\psi_{m\alpha}}^{(0)}\right\rangle + \cdots, \tag{3.60}$$

where

$$H'_{m\alpha;s} = \left\langle {\psi_{m\alpha}}^{(0)}\right| H' \left|{\psi_{s\alpha}}^{(0)}\right\rangle \tag{3.61}$$

When the perturbed state is also degenerate FIXME: diagram. states designated by dashes labeled $n1$, $n2$, $n3$ degeneracy $\alpha = 3$ for energy $E_n^{(0)}$, and states designated by dashes labeled $s1$, $s2$, $s3$ degeneracy $\alpha = 3$ for energy $E_s^{(0)}$.

If we just blindly repeat the derivation for the non-degenerate case we would obtain

$$E_s = E_s^{(0)} + \lambda H'_{s1;s1} + \lambda^2 \sum_{m\neq s,\alpha} \frac{\left|H'_{m\alpha;s1}\right|^2}{E_s^{(0)} - E_m^{(0)}} + \lambda^2 \sum_{\alpha\neq 1} \frac{\left|H'_{s\alpha;s1}\right|^2}{E_s^{(0)} - E_s^{(0)}} + \cdots \tag{3.62}$$

$$\left|\bar{\psi}_s\right\rangle = \left|{\psi_s}^{(0)}\right\rangle + \lambda \sum_{m\neq s,\alpha} \frac{H'_{m\alpha;s}}{E_s^{(0)} - E_m^{(0)}} \left|{\psi_{m\alpha}}^{(0)}\right\rangle + \lambda \sum_{\alpha\neq s1} \frac{H'_{s\alpha;s1}}{E_s^{(0)} - E_s^{(0)}} \left|{\psi_{s\alpha}}^{(0)}\right\rangle + \cdots, \tag{3.63}$$

where

$$H'_{m\alpha;s1} = \left\langle {\psi_{m\alpha}}^{(0)}\right| H' \left|{\psi_{s1}}^{(0)}\right\rangle \tag{3.64}$$

Note that the $E_s^{(0)} - E_s^{(0)}$ is NOT a typo, and why we run into trouble. There is one case where a perturbation approach is still possible. That case is if we happen to have

$$\left\langle {\psi_{m\alpha}}^{(0)}\right| H' \left|{\psi_{s1}}^{(0)}\right\rangle = 0. \tag{3.65}$$

That may not be obvious, but if one returns to the original derivation, the right terms cancel so that one will not end up with the $0/0$ problem.

FIXME: performing this derivation outside of class (below), it was found that we do not need the matrix elements of H' to be diagonal, but just need

$$\left\langle {\psi_{s\alpha}}^{(0)}\right| H' \left|{\psi_{s\beta}}^{(0)}\right\rangle = 0, \quad \text{for } \beta \neq \alpha. \tag{3.66}$$

That is consistent with problem set III where we did not diagonalize H', but just the subset of it associated with the degenerate states. I am unsure now if eq. (3.65) was copied in error or provided in error in class, but it definitely appears to be a more severe requirement than actually needed to deal with perturbation of a state found in a degenerate energy level.

3.2.0.7 *Time independent perturbation with degeneracy*

Now we repeat the derivation of the first order perturbation with degenerate states from lecture 4. We see explicitly how we would get into (divide by zero) trouble if the state we were perturbing had degeneracy. Here I alter the previous derivation to show this explicitly.

Like the non-degenerate case, we are covering the time independent perturbation methods from §16.1 of the text [4].

We start with a known Hamiltonian H_0, and alter it with the addition of a "small" perturbation

$$H = H_0 + \lambda H', \qquad \lambda \in [0, 1] \tag{3.67}$$

For the original operator, we assume that a complete set of eigenvectors and eigenkets is known

$$H_0 \left|\psi_{s\alpha}{}^{(0)}\right\rangle = E_s{}^{(0)} \left|\psi_{s\alpha}{}^{(0)}\right\rangle \tag{3.68}$$

We seek the perturbed eigensolution

$$H \left|\psi_{s\alpha}\right\rangle = E_{s\alpha} \left|\psi_{s\alpha}\right\rangle \tag{3.69}$$

and assumed a perturbative series representation for the energy eigenvalues in the new system

$$E_{s\alpha} = E_s{}^{(0)} + \lambda E_{s\alpha}{}^{(1)} + \lambda^2 E_{s\alpha}{}^{(2)} + \cdots \tag{3.70}$$

Note that we do not assume that the perturbed energy states, if degenerate in the original system, are still degenerate after perturbation.

Given an assumed representation for the new eigenkets in terms of the known basis

$$\left|\psi_{s\alpha}\right\rangle = \sum_{n,\beta} c_{ns;\beta\alpha} \left|\psi_{n\beta}{}^{(0)}\right\rangle \tag{3.71}$$

and a pertubative series representation for the probability coefficients

$$c_{ns;\beta\alpha} = c_{ns;\beta\alpha}{}^{(0)} + \lambda c_{ns;\beta\alpha}{}^{(1)} + \lambda^2 c_{ns;\beta\alpha}{}^{(2)}, \tag{3.72}$$

so that

$$|\psi_{s\alpha}\rangle = \sum_{n,\beta} {c_{ns;\beta\alpha}}^{(0)} \left|\psi_{n\beta}^{(0)}\right\rangle + \lambda \sum_{n,\beta} {c_{ns;\beta\alpha}}^{(1)} \left|\psi_{n\beta}^{(0)}\right\rangle + \lambda^2 \sum_{n,\beta} {c_{ns;\beta\alpha}}^{(2)} \left|\psi_{n\beta}^{(0)}\right\rangle + \cdots \tag{3.73}$$

Setting $\lambda = 0$ requires

$${c_{ns;\beta\alpha}}^{(0)} = \delta_{ns;\beta\alpha}, \tag{3.74}$$

for

$$\begin{aligned} |\psi_{s\alpha}\rangle &= \left|\psi_{s\alpha}^{(0)}\right\rangle + \lambda \sum_{n,\beta} {c_{ns;\beta\alpha}}^{(1)} \left|\psi_{n\beta}^{(0)}\right\rangle + \lambda^2 \sum_{n,\beta} {c_{ns;\beta\alpha}}^{(2)} \left|\psi_{n\beta}^{(0)}\right\rangle + \cdots \\ &= \left(1 + \lambda {c_{ss;\alpha\alpha}}^{(1)} + \lambda^2 {c_{ss;\alpha\alpha}}^{(2)} + \cdots\right) \left|\psi_{s\alpha}^{(0)}\right\rangle \\ &\quad + \lambda \sum_{n\beta \neq s\alpha} {c_{ns;\beta\alpha}}^{(1)} \left|\psi_{n\beta}^{(0)}\right\rangle \\ &\quad + \lambda^2 \sum_{n\beta \neq s\alpha} {c_{ns;\beta\alpha}}^{(2)} \left|\psi_{n\beta}^{(0)}\right\rangle + \cdots \end{aligned} \tag{3.75}$$

We rescale our kets

$$\left|\bar{\psi}_{s\alpha}\right\rangle = \left|\psi_{s\alpha}^{(0)}\right\rangle + \lambda \sum_{n\beta \neq s\alpha} {\bar{c}_{ns;\beta\alpha}}^{(1)} \left|\psi_{n\beta}^{(0)}\right\rangle + \lambda^2 \sum_{n\beta \neq s\alpha} {\bar{c}_{ns;\beta\alpha}}^{(2)} \left|\psi_{n\beta}^{(0)}\right\rangle + \cdots \tag{3.76}$$

where

$${\bar{c}_{ns;\beta\alpha}}^{(j)} = \frac{{c_{ns;\beta\alpha}}^{(j)}}{1 + \lambda {c_{ss;\alpha\alpha}}^{(1)} + \lambda^2 {c_{ss;\alpha\alpha}}^{(2)} + \cdots} \tag{3.77}$$

The normalization of the rescaled kets is then

$$\left\langle \bar{\psi}_{s\alpha} \middle| \bar{\psi}_{s\alpha} \right\rangle = 1 + \lambda^2 \sum_{n\beta \neq s\alpha} \left|{\bar{c}_{ss}}^{(1)}\right|^2 + \cdots \equiv \frac{1}{Z_{s\alpha}}, \tag{3.78}$$

One can then construct a renormalized ket if desired

$$\left|\bar{\psi}_{s\alpha}\right\rangle_R = Z_{s\alpha}^{1/2} \left|\bar{\psi}_{s\alpha}\right\rangle, \tag{3.79}$$

so that

$$(\left|\bar{\psi}_{s\alpha}\right\rangle_R)^\dagger \left|\bar{\psi}_{s\alpha}\right\rangle_R = Z_{s\alpha} \left\langle \bar{\psi}_{s\alpha} | \bar{\psi}_{s\alpha} \right\rangle = 1. \tag{3.80}$$

We continue by renaming terms in eq. (3.76)

$$\left|\bar{\psi}_{s\alpha}\right\rangle = \left|{\psi_{s\alpha}}^{(0)}\right\rangle + \lambda \left|{\psi_{s\alpha}}^{(1)}\right\rangle + \lambda^2 \left|{\psi_{s\alpha}}^{(2)}\right\rangle + \cdots \tag{3.81}$$

where

$$\left|{\psi_{s\alpha}}^{(j)}\right\rangle = \sum_{n\beta \neq s\alpha} \bar{c}_{ns;\beta\alpha}{}^{(j)} \left|\psi_{n\beta}{}^{(0)}\right\rangle. \tag{3.82}$$

Now we act on this with the Hamiltonian

$$H \left|\bar{\psi}_{s\alpha}\right\rangle = E_{s\alpha} \left|\bar{\psi}_{s\alpha}\right\rangle, \tag{3.83}$$

or

$$H \left|\bar{\psi}_{s\alpha}\right\rangle - E_{s\alpha} \left|\bar{\psi}_{s\alpha}\right\rangle = 0. \tag{3.84}$$

Expanding this, we have

$$\begin{aligned}(H_0 + \lambda H') &\left(\left|{\psi_{s\alpha}}^{(0)}\right\rangle + \lambda \left|{\psi_{s\alpha}}^{(1)}\right\rangle + \lambda^2 \left|{\psi_{s\alpha}}^{(2)}\right\rangle + \cdots\right) \\ &- \left(E_s{}^{(0)} + \lambda E_{s\alpha}{}^{(1)} + \lambda^2 E_{s\alpha}{}^{(2)} + \cdots\right)\left(\left|{\psi_{s\alpha}}^{(0)}\right\rangle + \lambda \left|{\psi_{s\alpha}}^{(1)}\right\rangle + \lambda^2 \left|{\psi_{s\alpha}}^{(2)}\right\rangle + \cdots\right) = 0.\end{aligned} \tag{3.85}$$

We want to write this as

$$|A\rangle + \lambda |B\rangle + \lambda^2 |C\rangle + \cdots = 0. \tag{3.86}$$

This is

$$\begin{aligned}0 = {} & \lambda^0 (H_0 - E_s^{(0)}) \left|{\psi_{s\alpha}}^{(0)}\right\rangle \\ & + \lambda \left((H_0 - E_s^{(0)}) \left|{\psi_{s\alpha}}^{(1)}\right\rangle + (H' - E_{s\alpha}^{(1)}) \left|{\psi_{s\alpha}}^{(0)}\right\rangle\right) \\ & + \lambda^2 \left((H_0 - E_s^{(0)}) \left|{\psi_{s\alpha}}^{(2)}\right\rangle + (H' - E_{s\alpha}^{(1)}) \left|{\psi_{s\alpha}}^{(1)}\right\rangle - E_{s\alpha}^{(2)} \left|{\psi_{s\alpha}}^{(0)}\right\rangle\right) \\ & \cdots\end{aligned} \tag{3.87}$$

So we form

$$\begin{aligned}
|A\rangle &= (H_0 - E_s^{(0)}) \left|\psi_{s\alpha}{}^{(0)}\right\rangle \\
|B\rangle &= (H_0 - E_s^{(0)}) \left|\psi_{s\alpha}{}^{(1)}\right\rangle + (H' - E_{s\alpha}^{(1)}) \left|\psi_{s\alpha}{}^{(0)}\right\rangle \\
|C\rangle &= (H_0 - E_s^{(0)}) \left|\psi_{s\alpha}{}^{(2)}\right\rangle + (H' - E_{s\alpha}^{(1)}) \left|\psi_{s\alpha}{}^{(1)}\right\rangle - E_{s\alpha}^{(2)} \left|\psi_{s\alpha}{}^{(0)}\right\rangle,
\end{aligned} \tag{3.88}$$

and so forth.

Zeroth order in λ Since $H_0 \left|\psi_{s\alpha}{}^{(0)}\right\rangle = E_s^{(0)} \left|\psi_{s\alpha}{}^{(0)}\right\rangle$, this first condition on $|A\rangle$ is not much more than a statement that $0 - 0 = 0$.

First order in λ How about $|B\rangle = 0$? For this to be zero we require that both of the following are simultaneously zero

$$\begin{aligned}
\left\langle\psi_{s\alpha}{}^{(0)}\right|B\rangle &= 0 \\
\left\langle\psi_{m\beta}{}^{(0)}\right|B\rangle &= 0, \qquad m\beta \neq s\alpha
\end{aligned} \tag{3.89}$$

This first condition is

$$\left\langle\psi_{s\alpha}{}^{(0)}\right| (H' - E_{s\alpha}^{(1)}) \left|\psi_{s\alpha}{}^{(0)}\right\rangle = 0. \tag{3.90}$$

With

$$\left\langle\psi_{m\beta}{}^{(0)}\right| H' \left|\psi_{s\alpha}{}^{(0)}\right\rangle \equiv H'_{ms;\beta\alpha}, \tag{3.91}$$

or

$$H'_{ss;\alpha\alpha} = E_{s\alpha}^{(1)}. \tag{3.92}$$

From the second condition we have

$$0 = \left\langle\psi_{m\beta}{}^{(0)}\right| (H_0 - E_s^{(0)}) \left|\psi_{s\alpha}{}^{(1)}\right\rangle + \left\langle\psi_{m\beta}{}^{(0)}\right| (H' - E_{s\alpha}^{(1)}) \left|\psi_{s\alpha}{}^{(0)}\right\rangle \tag{3.93}$$

Utilizing the Hermitian nature of H_0 we can act backwards on $\left\langle\psi_m{}^{(0)}\right|$

$$\left\langle\psi_{m\beta}{}^{(0)}\right| H_0 = E_m^{(0)} \left\langle\psi_{m\beta}{}^{(0)}\right|. \tag{3.94}$$

We note that $\left\langle\psi_{m\beta}{}^{(0)}\middle|\psi_{s\alpha}{}^{(0)}\right\rangle = 0, m\beta \neq s\alpha$. We can also expand the $\left\langle\psi_{m\beta}{}^{(0)}\middle|\psi_{s\alpha}{}^{(1)}\right\rangle$, which is

$$\left\langle\psi_{m\beta}{}^{(0)}\middle|\psi_{s\alpha}{}^{(1)}\right\rangle = \left\langle\psi_{m\beta}{}^{(0)}\right| \left(\sum_{n\delta \neq s\alpha} \bar{c}_{ns;\delta\alpha}{}^{(1)} \left|\psi_{n\delta}{}^{(0)}\right\rangle \right) \tag{3.95}$$

I found that reducing this sum was not obvious until some actual integers were plugged in. Suppose that $s = 3\,1$, and $m\beta = 2\,2$, then this is

$$\begin{aligned}\left\langle {\psi_{2\,2}}^{(0)} \middle| {\psi_{3\,1}}^{(1)} \right\rangle &= \left\langle {\psi_{2\,2}}^{(0)} \right| \left(\sum_{n\delta \in \{1\,1, 1\,2, \cdots, 2\,1, 2\,2, 2\,3, \cdots, 3\,2, 3\,3, \cdots\}} {\bar{c}_{n3;\delta 1}}^{(1)} \left| {\psi_{n\delta}}^{(0)} \right\rangle \right) \\ &= {\bar{c}_{2\,3;2\,1}}^{(1)} \left\langle {\psi_{2\,2}}^{(0)} \middle| {\psi_{2\,2}}^{(0)} \right\rangle \\ &= {\bar{c}_{2\,3;2\,1}}^{(1)}.\end{aligned} \tag{3.96}$$

Observe that we can also replace the superscript (1) with (j) in the above manipulation without impacting anything else. That and putting back in the abstract indices, we have the general result

$$\left\langle {\psi_{m\beta}}^{(0)} \middle| {\psi_{s\alpha}}^{(j)} \right\rangle = {\bar{c}_{ms;\beta\alpha}}^{(j)}. \tag{3.97}$$

Utilizing this gives us, for $m\beta \neq s\alpha$

$$0 = (E_m^{(0)} - E_s^{(0)}) {\bar{c}_{ms;\beta\alpha}}^{(1)} + {H'}_{ms;\beta\alpha} \tag{3.98}$$

Here we see our first sign of the trouble hinted at in lecture 5. Just because $m\beta \neq s\alpha$ does not mean that $m \neq s$. For example, with $m\beta = 1\,1$ and $s\alpha = 1\,2$ we would have

$$\begin{aligned} E_{12}^{(1)} &= {H'}_{1\,1;22} \\ {\bar{c}_{1\,1;12}}^{(1)} &= \frac{{H'}_{1\,1;12}}{E_1^{(0)} - E_1^{(0)}} \end{aligned} \tag{3.99}$$

We have got a divide by zero unless additional restrictions are imposed!

If we return to eq. (3.98), we see that, for the result to be valid, when $m = s$, and there exists degeneracy for the s state, we require for $\beta \neq \alpha$

$${H'}_{ss;\beta\alpha} = 0 \tag{3.100}$$

(then eq. (3.98) becomes a $0 = 0$ equality, and all is still okay)

And summarizing what we learn from our $|B\rangle = 0$ conditions we have

$$\begin{aligned} E_{s\alpha}^{(1)} &= {H'}_{ss;\alpha\alpha} \\ {\bar{c}_{ms;\beta\alpha}}^{(1)} &= \frac{{H'}_{ms;\beta\alpha}}{E_s^{(0)} - E_m^{(0)}}, \qquad m \neq s \\ {H'}_{ss;\beta\alpha} &= 0, \qquad \beta\alpha \neq 1\,1 \end{aligned} \tag{3.101}$$

Second order in λ Doing the same thing for $|C\rangle = 0$ we form (or assume)

$$\left\langle {\psi_{s\alpha}}^{(0)} \middle| C \right\rangle = 0 \tag{3.102}$$

$$\begin{aligned} 0 &= \left\langle {\psi_{s\alpha}}^{(0)} \middle| C \right\rangle \\ &= \left\langle {\psi_{s\alpha}}^{(0)} \middle| \left((H_0 - E_s^{(0)}) \left| {\psi_{s\alpha}}^{(2)} \right\rangle + (H' - E_{s\alpha}^{(1)}) \left| {\psi_{s\alpha}}^{(1)} \right\rangle - E_{s\alpha}^{(2)} \left| {\psi_{s\alpha}}^{(0)} \right\rangle \right) \right. \\ &= (E_s^{(0)} - E_s^{(0)}) \left\langle {\psi_{s\alpha}}^{(0)} \middle| {\psi_{s\alpha}}^{(2)} \right\rangle + \left\langle {\psi_{s\alpha}}^{(0)} \middle| (H' - E_{s\alpha}^{(1)}) \left| {\psi_{s\alpha}}^{(1)} \right\rangle - E_{s\alpha}^{(2)} \left\langle {\psi_{s\alpha}}^{(0)} \middle| {\psi_{s\alpha}}^{(0)} \right\rangle \end{aligned} \tag{3.103}$$

We need to know what the $\left\langle {\psi_{s\alpha}}^{(0)} \middle| {\psi_{s\alpha}}^{(1)} \right\rangle$ is, and find that it is zero

$$\left\langle {\psi_{s\alpha}}^{(0)} \middle| {\psi_{s\alpha}}^{(1)} \right\rangle = \left\langle {\psi_{s\alpha}}^{(0)} \right| \sum_{n\beta \neq s\alpha} {\bar{c}_{ns;\beta\alpha}}^{(1)} \left| {\psi_{n\beta}}^{(0)} \right\rangle = 0 \tag{3.104}$$

Utilizing that we have

$$\begin{aligned} E_{s\alpha}^{(2)} &= \left\langle {\psi_{s\alpha}}^{(0)} \right| H' \left| {\psi_{s\alpha}}^{(1)} \right\rangle \\ &= \left\langle {\psi_{s\alpha}}^{(0)} \right| H' \sum_{m\beta \neq s\alpha} {\bar{c}_{ms}}^{(1)} \left| {\psi_{m\beta}}^{(0)} \right\rangle \\ &= \sum_{m\beta \neq s\alpha} {\bar{c}_{ms;\beta\alpha}}^{(1)} {H'}_{sm;\alpha\beta} \end{aligned} \tag{3.105}$$

From eq. (3.101), treating the $m \neq s$ case carefully, we have

$$E_{s\alpha}^{(2)} = \sum_{\beta \neq \alpha} {\bar{c}_{ss;\beta\alpha}}^{(1)} {H'}_{ss;\alpha\beta} + \sum_{m\beta \neq s\alpha, m \neq s} \frac{{H'}_{ms;\beta\alpha}}{E_s^{(0)} - E_m^{(0)}} {H'}_{sm;\alpha\beta} \tag{3.106}$$

Again, only if $H_{ss;\alpha\beta} = 0$ for $\beta \neq \alpha$ do we have a result we can use. If that is the case, the first sum is killed without a divide by zero, leaving

$$E_{s\alpha}^{(2)} = \sum_{m\beta \neq s\alpha, m \neq s} \frac{\left| {H'}_{ms;\beta\alpha} \right|^2}{E_s^{(0)} - E_m^{(0)}}. \tag{3.107}$$

We can now summarize by forming the first order terms of the perturbed energy and the corresponding kets

$$\begin{aligned} E_{s\alpha} &= E_s^{(0)} + \lambda H'_{ss;\alpha\alpha} + \lambda^2 \sum_{m\neq s, m\beta\neq s\alpha} \frac{\left|H'_{ms;\beta\alpha}\right|^2}{E_s^{(0)} - E_m^{(0)}} + \cdots \\ \left|\bar{\psi}_{s\alpha}\right\rangle &= \left|{\psi_{s\alpha}}^{(0)}\right\rangle + \lambda \sum_{m\neq s, m\beta\neq s\alpha} \frac{H'_{ms;\beta\alpha}}{E_s^{(0)} - E_m^{(0)}} \left|{\psi_{m\beta}}^{(0)}\right\rangle + \cdots \\ H'_{ss;\beta\alpha} &= 0, \qquad \beta\alpha \neq 1\,1 \end{aligned} \tag{3.108}$$

Notational discrepancy: OOPS. It looks like I used different notation than in class for our matrix elements for the placement of the indices.

FIXME: looks like the ${c_{ss;\alpha\alpha'}}^{(1)}$, for $\alpha \neq \alpha'$ coeffients have been lost track of here? Do we have to assume those are zero too? Professor Sipe did not include those in his lecture eq. (3.114), but I do not see the motivation here for dropping them in this derivation.

Diagonalizing the perturbation Hamiltonian Suppose that we do not have this special zero condition that allows the perturbation treatment to remain valid. What can we do. It turns out that we can make use of the fact that the perturbation Hamiltonian is Hermitian, and diagonalize the matrix

$$\left\langle {\psi_{s\alpha}}^{(0)}\right| H' \left|{\psi_{s\beta}}^{(0)}\right\rangle \tag{3.109}$$

In the example of a two fold degeneracy, this amounts to us choosing not to work with the states

$$\left|\psi_{s1}^{(0)}\right\rangle, \left|\psi_{s2}^{(0)}\right\rangle, \tag{3.110}$$

both some linear combinations of the two

$$\left|\psi_{sI}^{(0)}\right\rangle = a_1 \left|\psi_{s1}^{(0)}\right\rangle + b_1 \left|\psi_{s2}^{(0)}\right\rangle \tag{3.111}$$

$$\left|\psi_{sII}^{(0)}\right\rangle = a_2 \left|\psi_{s1}^{(0)}\right\rangle + b_2 \left|\psi_{s2}^{(0)}\right\rangle \tag{3.112}$$

In this new basis, once found, we have

$$\left\langle {\psi_{s\alpha}}^{(0)}\right| H' \left|{\psi_{s\beta}}^{(0)}\right\rangle = \mathcal{H}_\alpha \delta_{\alpha\beta} \tag{3.113}$$

Utilizing this to fix the previous, one would get if the analysis was repeated correctly

$$E_{s\alpha} = E_s^{(0)} + \lambda H'_{s\alpha;s\alpha} + \lambda^2 \sum_{m\neq s,\beta} \frac{\left|H'_{m\beta;s\alpha}\right|^2}{E_s^{(0)} - E_m^{(0)}} + \cdots \tag{3.114}$$

$$\left|\bar{\psi}_{s\alpha}\right\rangle = \left|\psi_{s\alpha}{}^{(0)}\right\rangle + \lambda \sum_{m\neq s,\beta} \frac{H'_{m\beta;s\alpha}}{E_s^{(0)} - E_m^{(0)}} \left|\psi_{m\beta}{}^{(0)}\right\rangle + \cdots \tag{3.115}$$

FIXME: why do we have second order in λ terms for the energy when we found those exactly by diagonalization? We found there that the perturbed energy eigenvalues were multivalued with values $E_{s\alpha} = E_s^{(0)} + \lambda H'_{s\beta;s\beta}$ for all degeneracy indices β. Have to repeat the derivation for these more carefully to understand this apparent discrepancy.

We see that a degenerate state can be split by applying perturbation.

FIXME: diagram. $E_s^{(0)}$ as one energy level without perturbation, and as two distinct levels with perturbation.

guess I will bet that this is the origin of the spectral line splitting, especially given that an atom like hydrogen has degenerate states.

3.3 EXAMPLES

Example 3.1: Stark Shift

Reading: §16.5 of [4].

$$H = H_0 + \lambda H' \tag{3.116}$$

$$H' = e\mathcal{E}_z \hat{Z} \tag{3.117}$$

where $\mathcal{E}_z$ is the electric field.
To first order we have

$$\left|\psi_\alpha^{(1)}\right\rangle = \left|\psi_\alpha^{(0)}\right\rangle + \sum_{\beta\neq\alpha} \frac{\left|\psi_\beta^{(0)}\right\rangle \left\langle\psi_\beta^{(0)}\right| H' \left|\psi_\alpha^{(0)}\right\rangle}{E_\alpha^{(0)} - E_\beta^{(0)}} \tag{3.118}$$

and

$$E_\alpha^{(1)} = \left\langle \psi_\alpha^{(0)} \right| H' \left| \psi_\alpha^{(0)} \right\rangle \tag{3.119}$$

With the default basis $\{\left|\psi_\beta^{(0)}\right\rangle\}$, and $n = 2$ we have a 4 fold degeneracy

$$\begin{aligned} l, m &= 0, 0 \\ l, m &= 1, -1 \\ l, m &= 1, 0 \\ l, m &= 1, +1 \end{aligned} \tag{3.120}$$

but can diagonalize as follows

$$\begin{bmatrix} \text{nlm} & 200 & 210 & 211 & 21-1 \\ 200 & 0 & \Delta & 0 & 0 \\ 210 & \Delta & 0 & 0 & 0 \\ 211 & 0 & 0 & 0 & 0 \\ 21-1 & 0 & 0 & 0 & 0 \end{bmatrix} \tag{3.121}$$

FIXME: show.
where

$$\Delta = -3e\mathcal{E}_z a_0 \tag{3.122}$$

We have a split of energy levels as illustrated in fig. 3.2

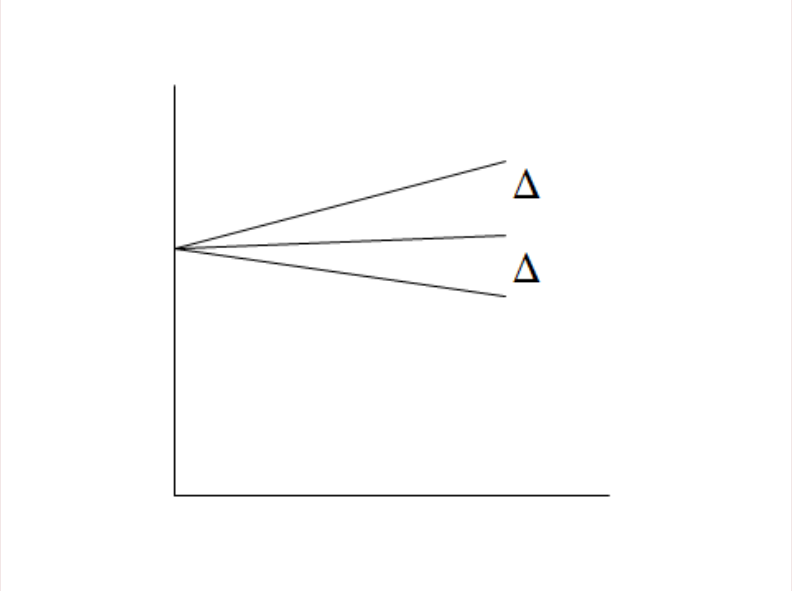

Figure 3.2: Energy level splitting

Observe the embedded Pauli matrix (FIXME: missed the point of this?)

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \tag{3.123}$$

Proper basis for perturbation (FIXME:check) is then

$$\left\{ \frac{1}{\sqrt{2}}(|2,0,0\rangle \pm |2,1,0\rangle), |2,1,\pm 1\rangle \right\} \tag{3.124}$$

and our result is

$$\left|\psi^{(1)}_{\alpha,n=2}\right\rangle = \left|\psi^{(0)}_{\alpha}\right\rangle + \sum_{\beta \notin \text{degenerate subspace}} \frac{\left|\psi^{(0)}_{\beta}\right\rangle \left\langle\psi^{(0)}_{\beta}\right| H' \left|\psi^{(0)}_{\alpha}\right\rangle}{E^{(0)}_{\alpha} - E^{(0)}_{\beta}} \tag{3.125}$$

4

TIME DEPENDENT PERTUBATION

4.1 REVIEW OF DYNAMICS

We want to move on to time dependent problems. In general for a time dependent problem, the answer follows provided one has solved for all the perturbed energy eigenvalues. This can be laborious (or not feasible due to infinite sums).

Before doing this, let us review our dynamics as covered in §3 of the text [4].

Schrödinger and Heisenberg pictures Our operator equation in the Schrödinger picture is the familiar

$$i\hbar\frac{d}{dt}\left|\psi_s(t)\right\rangle = H\left|\psi_s(t)\right\rangle \tag{4.1}$$

and most of our operators $X, P, \cdots$ are time independent.

$$\langle O\rangle(t) = \left\langle\psi_s(t)\right| O_s \left|\psi_s(t)\right\rangle \tag{4.2}$$

where O_s is the operator in the Schrödinger picture, and is non time dependent.
Formally, the time evolution of any state is given by

$$\left|\psi_s(t)\right\rangle e^{-iHt/\hbar}\left|\psi_s(0)\right\rangle = U(t,0)\left|\psi_s(0)\right\rangle \tag{4.3}$$

so the expectation of an operator can be written

$$\langle O\rangle(t) = \left\langle\psi_s(0)\right| e^{iHt/\hbar} O_s e^{-iHt/\hbar}\left|\psi_s(0)\right\rangle. \tag{4.4}$$

With the introduction of the Heisenberg ket

$$\left|\psi_H\right\rangle = \left|\psi_s(0)\right\rangle, \tag{4.5}$$

and Heisenberg operators

$$O_H = e^{iHt/\hbar} O_s e^{-iHt/\hbar}, \tag{4.6}$$

the expectation evolution takes the form

$$\langle O \rangle (t) = \langle \psi_H | O_H | \psi_H \rangle . \tag{4.7}$$

Note that because the Hamiltonian commutes with its exponential (it commutes with itself and any power series of itself), the Hamiltonian in the Heisenberg picture is the same as in the Schrödinger picture

$$H_H = e^{iHt/\hbar} H e^{-iHt/\hbar} = H. \tag{4.8}$$

Time evolution and the Commutator Taking the derivative of eq. (4.6) provides us with the time evolution of any operator in the Heisenberg picture

$$\begin{aligned} i\hbar \frac{d}{dt} O_H(t) &= i\hbar \frac{d}{dt} \left(e^{iHt/\hbar} O_s e^{-iHt/\hbar} \right) \\ &= i\hbar \left(\frac{iH}{\hbar} e^{iHt/\hbar} O_s e^{-iHt/\hbar} + e^{iHt/\hbar} O_s e^{-iHt/\hbar} \frac{-iH}{\hbar} \right) \\ &= \left(-H O_H + O_H H \right) . \end{aligned} \tag{4.9}$$

We can write this as a commutator

$$i\hbar \frac{d}{dt} O_H(t) = \left[O_H, H \right] . \tag{4.10}$$

Summarizing the two pictures

$$\begin{aligned} \text{Schrödinger picture} \qquad & \qquad \text{Heisenberg picture} \\ i\hbar \frac{d}{dt} |\psi_s(t)\rangle = H |\psi_s(t)\rangle \qquad & \qquad i\hbar \frac{d}{dt} O_H(t) = \left[O_H, H \right] \\ \langle \psi_s(t) | O_S | \psi_s(t) \rangle &= \langle \psi_H | O_H | \psi_H \rangle \\ |\psi_s(0)\rangle &= |\psi_H\rangle \\ O_S &= O_H(0) \end{aligned} \tag{4.11}$$

4.2 INTERACTION PICTURE

Recap Recall our table comparing our two interaction pictures

$$\begin{aligned} \text{Schrödinger picture} \qquad & \qquad \text{Heisenberg picture} \\ i\hbar \frac{d}{dt} |\psi_s(t)\rangle = H |\psi_s(t)\rangle \qquad & \qquad i\hbar \frac{d}{dt} O_H(t) = [O_H, H] \\ \langle \psi_s(t)| O_S |\psi_s(t)\rangle &= \langle \psi_H| O_H |\psi_H\rangle \\ |\psi_s(0)\rangle &= |\psi_H\rangle \\ O_S &= O_H(0) \end{aligned} \tag{4.12}$$

A motivating example While fundamental Hamiltonians are independent of time, in a number of common cases, we can form approximate Hamiltonians that are time dependent. One such example is that of Coulomb excitations of an atom, as covered in §18.3 of the text [4], and shown in fig. 4.1.

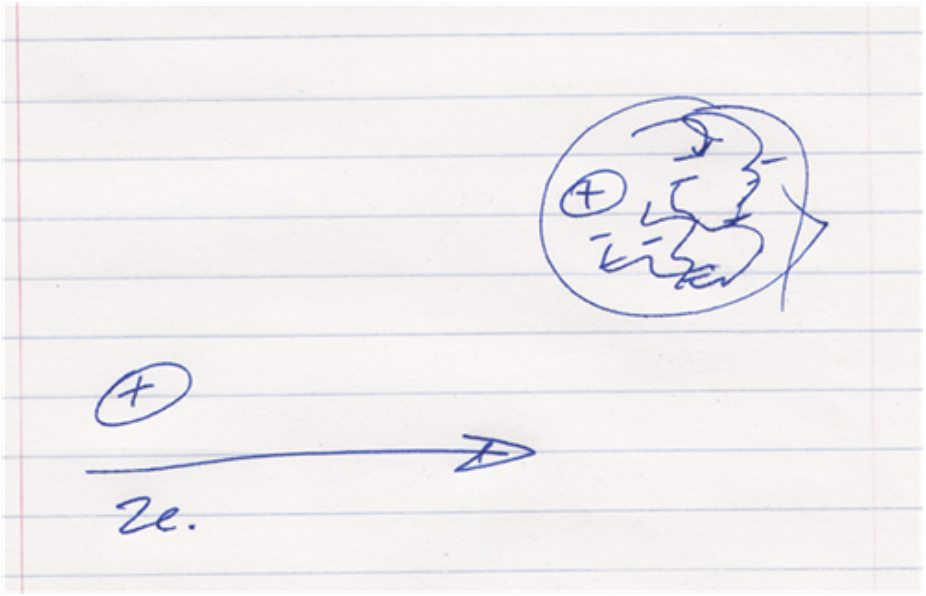

Figure 4.1: Coulomb interaction of a nucleus and heavy atom

We consider the interaction of a nucleus with a neutral atom, heavy enough that it can be considered classically. From the atoms point of view, the effects of the heavy nucleus barrel-

ing by can be described using a time dependent Hamiltonian. For the atom, that interaction Hamiltonian is

$$H' = \sum_i \frac{Zeq_i}{|\mathbf{r}_N(t) - \mathbf{R}_i|}. \tag{4.13}$$

Here and $\mathbf{r}_N$ is the position vector for the heavy nucleus, and $\mathbf{R}_i$ is the position to each charge within the atom, where i ranges over all the internal charges, positive and negative, within the atom.

Placing the origin close to the atom, we can write this interaction Hamiltonian as

$$H'(t) = \cancel{\sum_i \frac{Zeq_i}{|\mathbf{r}_N(t)|}} + \sum_i Zeq_i \mathbf{R}_i \cdot \left(\frac{\partial}{\partial \mathbf{r}} \frac{1}{|\mathbf{r}_N(t) - \mathbf{r}|} \right) \Bigg|_{\mathbf{r}=0} \tag{4.14}$$

The first term vanishes because the total charge in our neutral atom is zero. This leaves us with

$$\begin{aligned} H'(t) &= -\sum_i q_i \mathbf{R}_i \cdot \left(-\frac{\partial}{\partial \mathbf{r}} \frac{Ze}{|\mathbf{r}_N(t) - \mathbf{r}|} \right) \Bigg|_{\mathbf{r}=0} \\ &= -\sum_i q_i \mathbf{R}_i \cdot \mathbf{E}(t), \end{aligned} \tag{4.15}$$

where $\mathbf{E}(t)$ is the electric field at the origin due to the nucleus.

Introducing a dipole moment operator for the atom

$$\boldsymbol{\mu} = \sum_i q_i \mathbf{R}_i, \tag{4.16}$$

the interaction takes the form

$$H'(t) = -\boldsymbol{\mu} \cdot \mathbf{E}(t). \tag{4.17}$$

Here we have a quantum mechanical operator, and a classical field taken together. This sort of dipole interaction also occurs when we treat a atom placed into an electromagnetic field, treated classically as depicted in fig. 4.2

In the figure, we can use the dipole interaction, provided $\lambda \gg a$, where a is the "width" of the atom.

Because it is great for examples, we will see this dipole interaction a lot.

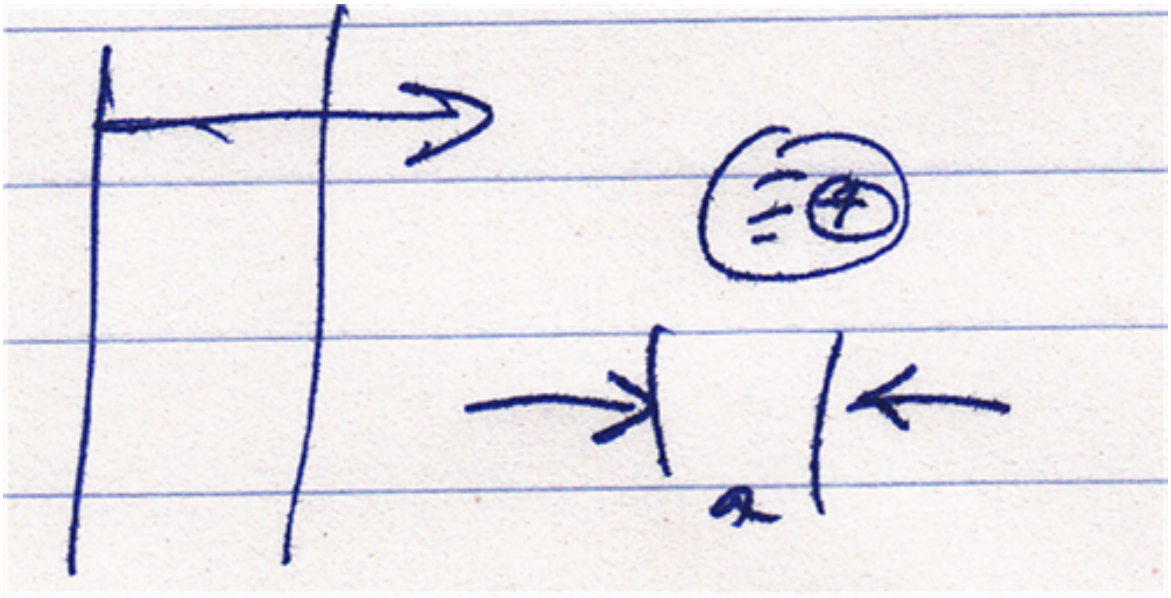

Figure 4.2: atom in a field

The interaction picture Having talked about both the Schrödinger and Heisenberg pictures, we can now move on to describe a hybrid, one where our Hamiltonian has been split into static and time dependent parts

$$H(t) = H_0 + H'(t) \tag{4.18}$$

We will formulate an approach for dealing with problems of this sort called the interaction picture.

This is also covered in §3.3 of the text, albeit in a much harder to understand fashion (the text appears to try to not pull the result from a magic hat, but the steps to get to the end result are messy). It would probably have been nicer to see it this way instead.

In the Schrödinger picture our dynamics have the form

$$i\hbar \frac{d}{dt} |\psi_s(t)\rangle = H |\psi_s(t)\rangle \tag{4.19}$$

How about the Heisenberg picture? We look for a solution

$$|\psi_s(t)\rangle = U(t, t_0) |\psi_s(t_0)\rangle \,. \tag{4.20}$$

We want to find this operator that evolves the state from the state as some initial time t_0, to the arbitrary later state found at time t. Plugging in we have

$$i\hbar\frac{d}{dt}U(t,t_0)\,|\psi_s(t_0)\rangle = H(t)U(t,t_0)\,|\psi_s(t_0)\rangle\,. \tag{4.21}$$

This has to hold for all $|\psi_s(t_0)\rangle$, and we can equivalently seek a solution of the operator equation

$$i\hbar\frac{d}{dt}U(t,t_0) = H(t)U(t,t_0), \tag{4.22}$$

where

$$U(t_0,t_0) = I, \tag{4.23}$$

the identity for the Hilbert space.
Suppose that $H(t)$ was independent of time. We could find that

$$U(t,t_0) = e^{-iH(t-t_0)/\hbar}. \tag{4.24}$$

If $H(t)$ depends on time could you guess that

$$U(t,t_0) = e^{-\frac{i}{\hbar}\int_{t_0}^{t}H(\tau)d\tau} \tag{4.25}$$

holds? No. This may be true when $H(t)$ is a number, but when it is an operator, the Hamiltonian does not necessarily commute with itself at different times

$$[H(t'),H(t'')] \neq 0. \tag{4.26}$$

So this is wrong in general. As an aside, for numbers, eq. (4.25) can be verified easily. We have

$$\begin{aligned} i\hbar\left(e^{-\frac{i}{\hbar}\int_{t_0}^{t}H(\tau)d\tau}\right)' &= i\hbar\left(-\frac{i}{\hbar}\right)\left(\int_{t_0}^{t}H(\tau)d\tau\right)' e^{-\frac{i}{\hbar}\int_{t_0}^{t}H(\tau)d\tau} \\ &= \left(H(t)\frac{dt}{dt} - H(t_0)\frac{dt_0}{dt}\right)e^{-\frac{i}{\hbar}\int_{t_0}^{t}H(\tau)d\tau} \\ &= H(t)U(t,t_0) \end{aligned} \tag{4.27}$$

Expectations Suppose that we do find $U(t, t_0)$. Then our expectation takes the form

$$\langle \psi_s(t)| O_s |\psi_s(t)\rangle = \langle \psi_s(t_0)| U^\dagger(t, t_0) O_s U(t, t_0) |\psi_s(t_0)\rangle \tag{4.28}$$

Put

$$|\psi_H\rangle = |\psi_s(t_0)\rangle\,, \tag{4.29}$$

and form

$$O_H = U^\dagger(t, t_0) O_s U(t, t_0) \tag{4.30}$$

so that our expectation has the familiar representations

$$\langle \psi_s(t)| O_s |\psi_s(t)\rangle = \langle \psi_H| O_H |\psi_H\rangle \tag{4.31}$$

New strategy. Interaction picture Let us define

$$U_I(t, t_0) = e^{\frac{i}{\hbar} H_0 (t - t_0)} U(t, t_0) \tag{4.32}$$

or

$$U(t, t_0) = e^{-\frac{i}{\hbar} H_0 (t - t_0)} U_I(t, t_0). \tag{4.33}$$

Let us see how this works. We have

$$\begin{aligned} i\hbar \frac{dU_I}{dt} &= i\hbar \frac{d}{dt} \left(e^{\frac{i}{\hbar} H_0 (t - t_0)} U(t, t_0) \right) \\ &= -H_0 U(t, t_0) + e^{\frac{i}{\hbar} H_0 (t - t_0)} \left(i\hbar \frac{d}{dt} U(t, t_0) \right) \\ &= -H_0 U(t, t_0) + e^{\frac{i}{\hbar} H_0 (t - t_0)} \left((H + H'(t)) U(t, t_0) \right) \\ &= e^{\frac{i}{\hbar} H_0 (t - t_0)} H'(t) U(t, t_0) \\ &= e^{\frac{i}{\hbar} H_0 (t - t_0)} H'(t) e^{-\frac{i}{\hbar} H_0 (t - t_0)} U_I(t, t_0). \end{aligned} \tag{4.34}$$

Define

$$\overline{H}'(t) = e^{\frac{i}{\hbar} H_0 (t - t_0)} H'(t) e^{-\frac{i}{\hbar} H_0 (t - t_0)}, \tag{4.35}$$

so that our operator equation takes the form

$$i\hbar\frac{d}{dt}U_I(t,t_0) = \overline{H}'(t)U_I(t,t_0). \tag{4.36}$$

Note that we also have the required identity at the initial time

$$U_I(t_0,t_0) = I. \tag{4.37}$$

Without requiring us to actually find $U(t,t_0)$ all of the dynamics of the time dependent interaction are now embedded in our operator equation for $\overline{H}'(t)$, with all of the simple interaction related to the non time dependent portions of the Hamiltonian left separate.

Connection with the Schrödinger picture In the Schrödinger picture we have

$$\begin{aligned}|\psi_s(t)\rangle &= U(t,t_0)\,|\psi_s(t_0)\rangle \\ &= e^{-\frac{i}{\hbar}H_0(t-t_0)}U_I(t,t_0)\,|\psi_s(t_0)\rangle\,.\end{aligned} \tag{4.38}$$

With a definition of the interaction picture ket as

$$|\psi_I\rangle = U_I(t,t_0)\,|\psi_s(t_0)\rangle = U_I(t,t_0)\,|\psi_H\rangle\,, \tag{4.39}$$

the Schrödinger picture is then related to the interaction picture by

$$|\psi_s(t)\rangle = e^{-\frac{i}{\hbar}H_0(t-t_0)}\,|\psi_I\rangle\,. \tag{4.40}$$

Also, by multiplying eq. (4.36) by our Schrödinger ket, we remove the last vestiges of U_I and U from the dynamical equation for our time dependent interaction

$$i\hbar\frac{d}{dt}\,|\psi_I\rangle = \overline{H}'(t)\,|\psi_I\rangle\,. \tag{4.41}$$

Interaction picture expectation Inverting eq. (4.40), we can form an operator expectation, and relate it the interaction and Schrödinger pictures

$$\langle\psi_s(t)|\,O_s\,|\psi_s(t)\rangle = \langle\psi_I|\,e^{\frac{i}{\hbar}H_0(t-t_0)}O_s e^{-\frac{i}{\hbar}H_0(t-t_0)}\,|\psi_I\rangle\,. \tag{4.42}$$

With a definition

$$O_I = e^{\frac{i}{\hbar}H_0(t-t_0)} O_s e^{-\frac{i}{\hbar}H_0(t-t_0)}, \tag{4.43}$$

we have

$$\langle\psi_s(t)|\, O_s\, |\psi_s(t)\rangle = \langle\psi_I|\, O_I\, |\psi_I\rangle\,. \tag{4.44}$$

As before, the time evolution of our interaction picture operator, can be found by taking derivatives of eq. (4.43), for which we find

$$i\hbar\frac{dO_I(t)}{dt} = [O_I(t), H_0] \tag{4.45}$$

Summarizing the interaction picture Given

$$H(t) = H_0 + H'(t), \tag{4.46}$$

and initial time states

$$|\psi_I(t_0)\rangle = |\psi_s(t_0)\rangle = |\psi_H\rangle\,, \tag{4.47}$$

we have

$$\langle\psi_s(t)|\, O_s\, |\psi_s(t)\rangle = \langle\psi_I|\, O_I\, |\psi_I\rangle\,, \tag{4.48}$$

where

$$|\psi_I\rangle = U_I(t, t_0)\, |\psi_s(t_0)\rangle\,, \tag{4.49}$$

and

$$i\hbar\frac{d}{dt}\,|\psi_I\rangle = \overline{H}'(t)\,|\psi_I\rangle\,, \tag{4.50}$$

or

$$\begin{aligned} i\hbar\frac{d}{dt}U_I(t, t_0) &= \overline{H}'(t)U_I(t, t_0) \\ U_I(t_0, t_0) &= I. \end{aligned} \tag{4.51}$$

Our interaction picture Hamiltonian is

$$\overline{H}'(t) = e^{\frac{i}{\hbar}H_0(t-t_0)}H'(t)e^{-\frac{i}{\hbar}H_0(t-t_0)}, \tag{4.52}$$

and for Schrödinger operators, independent of time, we have the dynamical equation

$$i\hbar\frac{dO_I(t)}{dt} = [O_I(t), H_0] \tag{4.53}$$

4.3 JUSTIFYING THE TAYLOR EXPANSION ABOVE (NOT CLASS NOTES)

Multivariable Taylor series As outlined in §2.8 (8.10) of [7], we want to derive the multivariable Taylor expansion for a scalar valued function of some number of variables

$$f(\mathbf{u}) = f(u^1, u^2, \cdots), \tag{4.54}$$

consider the displacement operation applied to the vector argument

$$f(\mathbf{a} + \mathbf{x}) = f(\mathbf{a} + t\mathbf{x})|_{t=1}. \tag{4.55}$$

We can Taylor expand a single variable function without any trouble, so introduce

$$g(t) = f(\mathbf{a} + t\mathbf{x}), \tag{4.56}$$

where

$$g(1) = f(\mathbf{a} + \mathbf{x}). \tag{4.57}$$

We have

$$g(t) = g(0) + t\left.\frac{\partial g}{\partial t}\right|_{t=0} + \frac{t^2}{2!}\left.\frac{\partial g}{\partial t}\right|_{t=0} + \cdots, \tag{4.58}$$

so that

$$g(1) = g(0) + + \left.\frac{\partial g}{\partial t}\right|_{t=0} + \frac{1}{2!}\left.\frac{\partial g}{\partial t}\right|_{t=0} + \cdots. \tag{4.59}$$

The multivariable Taylor series now becomes a plain old application of the chain rule, where we have to evaluate

$$\begin{aligned}\frac{dg}{dt} &= \frac{d}{dt} f(a^1 + tx^1, a^2 + tx^2, \cdots) \\ &= \sum_i \frac{\partial}{\partial(a^i + tx^i)} f(\mathbf{a} + t\mathbf{x}) \frac{\partial a^i + tx^i}{\partial t},\end{aligned} \tag{4.60}$$

so that

$$\left.\frac{dg}{dt}\right|_{t=0} = \sum_i x^i \left(\left.\frac{\partial f}{\partial x^i}\right|_{x^i = a^i} \right). \tag{4.61}$$

Assuming an Euclidean space we can write this in the notationally more pleasant fashion using a gradient operator for the space

$$\left.\frac{dg}{dt}\right|_{t=0} = \mathbf{x} \cdot \boldsymbol{\nabla}_{\mathbf{u}} f(\mathbf{u})|_{\mathbf{u}=\mathbf{a}}. \tag{4.62}$$

To handle the higher order terms, we repeat the chain rule application, yielding for example

$$\begin{aligned}\left.\frac{d^2 f(\mathbf{a} + t\mathbf{x})}{dt^2}\right|_{t=0} &= \left.\frac{d}{dt} \sum_i x^i \frac{\partial f(\mathbf{a} + t\mathbf{x})}{\partial(a^i + tx^i)}\right|_{t=0} \\ &= \left.\sum_i x^i \frac{\partial}{\partial(a^i + tx^i)} \frac{df(\mathbf{a} + t\mathbf{x})}{dt}\right|_{t=0} \\ &= (\mathbf{x} \cdot \boldsymbol{\nabla}_{\mathbf{u}})^2 f(\mathbf{u})\big|_{\mathbf{u}=\mathbf{a}}.\end{aligned} \tag{4.63}$$

Thus the Taylor series associated with a vector displacement takes the tidy form

$$f(\mathbf{a} + \mathbf{x}) = \sum_{k=0}^{\infty} \frac{1}{k!} (\mathbf{x} \cdot \boldsymbol{\nabla}_{\mathbf{u}})^k f(\mathbf{u})\big|_{\mathbf{u}=\mathbf{a}}. \tag{4.64}$$

Even more fancy, we can form the operator equation

$$f(\mathbf{a} + \mathbf{x}) = e^{\mathbf{x} \cdot \boldsymbol{\nabla}_{\mathbf{u}}} f(\mathbf{u})\big|_{\mathbf{u}=\mathbf{a}} \tag{4.65}$$

Here a dummy variable $\mathbf{u}$ has been retained as an instruction not to differentiate the $\mathbf{x}$ part of the directional derivative in any repeated applications of the $\mathbf{x} \cdot \boldsymbol{\nabla}$ operator.

That notational cludge can be removed by swapping **a** and **x**

$$f(\mathbf{a}+\mathbf{x}) = \sum_{k=0}^{\infty} \frac{1}{k!}(\mathbf{a}\cdot\boldsymbol{\nabla})^k f(\mathbf{x}) = e^{\mathbf{a}\cdot\boldsymbol{\nabla}} f(\mathbf{x}), \tag{4.66}$$

where $\boldsymbol{\nabla} = \boldsymbol{\nabla}_{\mathbf{x}} = (\partial/\partial x^1, \partial/\partial x^2, ...)$.

Having derived this (or for those with lesser degrees of amnesia, recall it), we can see that eq. (4.14) was a direct application of this, retaining no second order or higher terms.

Our expression used in the interaction Hamiltonian discussion was

$$\frac{1}{|\mathbf{r}-\mathbf{R}|} \approx \frac{1}{|\mathbf{r}|} + \mathbf{R}\cdot\left(\frac{\partial}{\partial\mathbf{R}}\frac{1}{|\mathbf{r}-\mathbf{R}|}\right)\Bigg|_{\mathbf{R}=0}. \tag{4.67}$$

which we can see has the same structure as above with some variable substitutions. Evaluating it we have

$$\begin{aligned}\frac{\partial}{\partial\mathbf{R}}\frac{1}{|\mathbf{r}-\mathbf{R}|} &= \mathbf{e}_i\frac{\partial}{\partial R^i}((x^j-R^j)^2)^{-1/2} \\ &= \mathbf{e}_i\left(-\frac{1}{2}\right)2(x^j-R^j)\frac{\partial(x^j-R^j)}{\partial R^i}\frac{1}{|\mathbf{r}-\mathbf{R}|^3} \\ &= \frac{\mathbf{r}-\mathbf{R}}{|\mathbf{r}-\mathbf{R}|^3},\end{aligned} \tag{4.68}$$

and at $\mathbf{R} = 0$ we have

$$\frac{1}{|\mathbf{r}-\mathbf{R}|} \approx \frac{1}{|\mathbf{r}|} + \mathbf{R}\cdot\frac{\mathbf{r}}{|\mathbf{r}|^3}. \tag{4.69}$$

We see in this direction derivative produces the classical electric Coulomb field expression for an electrostatic distribution, once we take the $\mathbf{r}/|\mathbf{r}|^3$ and multiply it with the $-Ze$ factor.

With algebra A different way to justify the expansion of eq. (4.14) is to consider a Clifford algebra factorization (following notation from [5]) of the absolute vector difference, where $\mathbf{R}$ is considered small.

$$\begin{aligned}
|\mathbf{r}-\mathbf{R}| &= \sqrt{(\mathbf{r}-\mathbf{R})\,(\mathbf{r}-\mathbf{R})} \\
&= \sqrt{\left\langle \mathbf{r}\left(1-\frac{1}{\mathbf{r}}\mathbf{R}\right)\left(1-\mathbf{R}\frac{1}{\mathbf{r}}\right)\mathbf{r}\right\rangle} \\
&= \sqrt{\left\langle \mathbf{r}^2\left(1-\frac{1}{\mathbf{r}}\mathbf{R}\right)\left(1-\mathbf{R}\frac{1}{\mathbf{r}}\right)\right\rangle} \\
&= |\mathbf{r}|\sqrt{1-2\frac{1}{\mathbf{r}}\cdot\mathbf{R}+\left\langle\frac{1}{\mathbf{r}}\mathbf{R}\mathbf{R}\frac{1}{\mathbf{r}}\right\rangle} \\
&= |\mathbf{r}|\sqrt{1-2\frac{1}{\mathbf{r}}\cdot\mathbf{R}+\frac{\mathbf{R}^2}{\mathbf{r}^2}}
\end{aligned} \tag{4.70}$$

Neglecting the $\mathbf{R}^2$ term, we can then Taylor series expand this scalar expression

$$\frac{1}{|\mathbf{r}-\mathbf{R}|} \approx \frac{1}{|\mathbf{r}|}\left(1+\frac{1}{\mathbf{r}}\cdot\mathbf{R}\right) = \frac{1}{|\mathbf{r}|}+\frac{\hat{\mathbf{r}}}{\mathbf{r}^2}\cdot\mathbf{R} = \frac{1}{|\mathbf{r}|}+\frac{\mathbf{r}}{|\mathbf{r}|^3}\cdot\mathbf{R}. \tag{4.71}$$

Observe this is what was found with the multivariable Taylor series expansion too.

4.4 RECAP: INTERACTION PICTURE

We will use the interaction picture to examine time dependent perturbations. We wrote our Schrödinger ket in terms of the interaction ket

$$|\psi\rangle = e^{-iH_0(t-t_0)/\hbar}\,|\psi_I(t)\rangle\,, \tag{4.72}$$

where

$$|\psi_I\rangle = U_I(t,t_0)\,|\psi_I(t_0)\rangle\,. \tag{4.73}$$

Our dynamics is given by the operator equation

$$i\hbar\frac{d}{dt}U_I(t,t_0) = \overline{H}'(t)U_I(t,t_0), \tag{4.74}$$

where

$$\overline{H}'(t) = e^{\frac{i}{\hbar}H_0(t-t_0)}H'(t)e^{-\frac{i}{\hbar}H_0(t-t_0)}. \tag{4.75}$$

We can formally solve eq. (4.74) by writing

$$U_I(t,t_0) = I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\overline{H}'(t')U_I(t',t_0). \tag{4.76}$$

This is easy enough to verify by direct differentiation

$$\begin{aligned} i\hbar\frac{d}{dt}U_I &= \left(\int_{t_0}^{t} dt'\overline{H}'(t')U_I(t',t_0)\right)' \\ &= \overline{H}'(t)U_I(t,t_0)\frac{dt}{dt} - \overline{H}'(t)U_I(t,t_0)\frac{dt_0}{dt} \\ &= \overline{H}'(t)U_I(t,t_0) \end{aligned} \tag{4.77}$$

This is a bit of a chicken and an egg expression, since it is cyclic with a dependency on unknown $U_I(t',t_0)$ factors.

We start with an initial estimate of the operator to be determined, and iterate. This can seem like an odd thing to do, but one can find books on just this integral kernel iteration method (like the nice little Dover book [13] that has sat on my (Peeter's) shelf all lonely so many years).

Suppose for t near t_0, try

$$U_I(t,t_0) \approx I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\overline{H}'(t'). \tag{4.78}$$

A second order iteration is now possible

$$\begin{aligned} U_I(t,t_0) &\approx I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\overline{H}'(t')\left(I - \frac{i}{\hbar}\int_{t_0}^{t'} dt''\overline{H}'(t'').\right) \\ &= I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\overline{H}'(t') + \left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t} dt'\overline{H}'(t')\int_{t_0}^{t'} dt''\overline{H}'(t'') \end{aligned} \tag{4.79}$$

It is possible to continue this iteration, and this approach is considered in some detail in §3.3 of the text [4], and is apparently also the basis for Feynman diagrams.

4.5 TIME DEPENDENT PERTURBATION THEORY

As covered in §17 of the text, we will split the interaction into time independent and time dependent terms

$$H(t) = H_0 + H'(t), \tag{4.80}$$

and work in the interaction picture with

$$|\psi_I(t)\rangle = \sum_n \tilde{c}_n(t) \left|\psi_n^{(0)}\right\rangle. \tag{4.81}$$

Our Schrödinger ket is then

$$\begin{aligned} |\psi(t)\rangle &= e^{-iH_0^{(0)}(t-t_0)/\hbar} |\psi_I(t_0)\rangle \\ &= \sum_n \tilde{c}_n(t) e^{-iE_n^{(0)}(t-t_0)/\hbar} \left|\psi_n^{(0)}\right\rangle. \end{aligned} \tag{4.82}$$

With a definition

$$c_n(t) = \tilde{c}_n(t) e^{iE_n t_0/\hbar}, \tag{4.83}$$

(where we leave off the zero superscript for the unperturbed state), our time evolved ket becomes

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-iE_n t/\hbar} \left|\psi_n^{(0)}\right\rangle. \tag{4.84}$$

We can now plug eq. (4.81) into our evolution equation

$$\begin{aligned} i\hbar \frac{d}{dt} |\psi_I(t)\rangle &= \overline{H}'(t) |\psi_I(t)\rangle \\ &= e^{\frac{i}{\hbar}H_0(t-t_0)} H'(t) e^{-\frac{i}{\hbar}H_0(t-t_0)} |\psi_I(t)\rangle, \end{aligned} \tag{4.85}$$

which gives us

$$i\hbar \sum_p \frac{\partial}{\partial t} \tilde{c}_p(t) \left|\psi_p^{(0)}\right\rangle = e^{\frac{i}{\hbar}H_0(t-t_0)} H'(t) e^{-\frac{i}{\hbar}H_0(t-t_0)} \sum_n \tilde{c}_n(t) \left|\psi_n^{(0)}\right\rangle. \tag{4.86}$$

We can apply the bra $\left\langle \psi_m^{(0)} \right|$ to this equation, yielding

$$i\hbar \frac{\partial}{\partial t} \tilde{c}_m(t) = \sum_n \tilde{c}_n(t) e^{\frac{i}{\hbar} E_m (t-t_0)} \left\langle \psi_m^{(0)} \right| H'(t) \left| \psi_n^{(0)} \right\rangle e^{-\frac{i}{\hbar} E_n (t-t_0)}. \tag{4.87}$$

With

$$\begin{aligned} \omega_m &= \frac{E_m}{\hbar} \\ \omega_{mn} &= \omega_m - \omega_n \\ H'_{mn}(t) &= \left\langle \psi_m^{(0)} \right| H'(t) \left| \psi_n^{(0)} \right\rangle, \end{aligned} \tag{4.88}$$

this is

$$i\hbar \frac{\partial \tilde{c}_m(t)}{\partial t} = \sum_n \tilde{c}_n(t) e^{i\omega_{mn}(t-t_0)} H'_{mn}(t) \tag{4.89}$$

Inverting eq. (4.83) and plugging in

$$\tilde{c}_n(t) = c_n(t) e^{-i\omega_n t_0}, \tag{4.90}$$

yields

$$i\hbar \frac{\partial c_m(t)}{\partial t} e^{-i\omega_m t_0} = \sum_n c_n(t) e^{-i\omega_n t_0} e^{i\omega_{mn} t} e^{-i(\omega_m - \omega_n) t_0} H'_{mn}(t), \tag{4.91}$$

from which we can cancel the exponentials on both sides yielding

$$i\hbar \frac{\partial c_m(t)}{\partial t} = \sum_n c_n(t) e^{i\omega_{mn} t} H'_{mn}(t) \tag{4.92}$$

We are now left with all of our time dependence nicely separated out, with the coefficients $c_n(t)$ encoding all the non-oscillatory time evolution information

$$\begin{aligned} H &= H_0 + H'(t) \\ |\psi(t)\rangle &= \sum_n c_n(t) e^{-i\omega_n t} \left| \psi_n^{(0)} \right\rangle \\ i\hbar \dot{c}_m &= \sum_n H'_{mn}(t) e^{i\omega_{mn} t} c_n(t) \end{aligned} \tag{4.93}$$

4.6 PERTURBATION EXPANSION

We now introduce our λ parametrization

$$H'(t) \to \lambda H'(t), \tag{4.94}$$

and hope for convergence, or at least something that at least has well defined asymptotic behavior. We have

$$i\hbar \dot{c}_m = \lambda \sum_n H'_{mn}(t) e^{i\omega_{mn}t} c_n(t), \tag{4.95}$$

and try

$$c_m(t) = c_m^{(0)}(t) + \lambda c_m^{(1)}(t) + \lambda^2 c_m^{(2)}(t) + \cdots \tag{4.96}$$

Plugging in, we have

$$i\hbar \sum_k \lambda^k \dot{c}_m^{(k)}(t) = \sum_{n,p} H'_{mn}(t) e^{i\omega_{mn}t} \lambda^{p+1} c_n^{(p)}(t). \tag{4.97}$$

As before, for equality, we treat this as an equation for each λ^k. Expanding explicitly for the first few powers, gives us

$$\begin{aligned} 0 &= \lambda^0 \left(i\hbar \dot{c}_m^{(0)}(t) - 0 \right) \\ &+ \lambda^1 \left(i\hbar \dot{c}_m^{(1)}(t) - \sum_n H'_{mn}(t) e^{i\omega_{mn}t} c_n^{(0)}(t) \right) \\ &+ \lambda^2 \left(i\hbar \dot{c}_m^{(2)}(t) - \sum_n H'_{mn}(t) e^{i\omega_{mn}t} c_n^{(1)}(t) \right) \\ &\vdots \end{aligned} \tag{4.98}$$

Suppose we have a set of energy levels as depicted in fig. 4.3

With $c_n^{(i)} = 0$ before the perturbation for all $i \geq 1, n$ and $c_m^{(0)} = \delta_{ms}$, we can proceed iteratively, solving each equation, starting with

$$i\hbar \dot{c}_m^{(1)} = H'_{ms}(t) e^{i\omega_{ms}t} \tag{4.99}$$

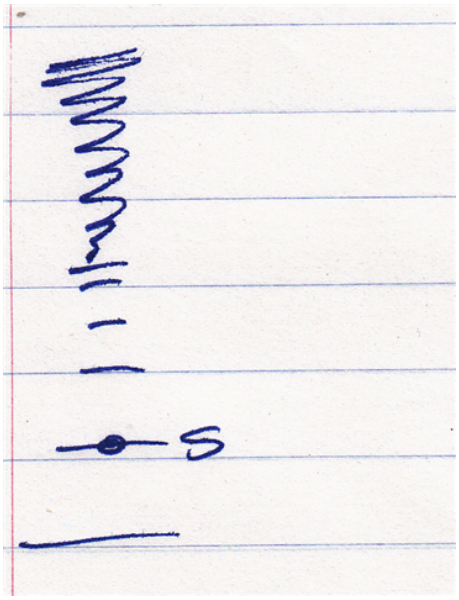

Figure 4.3: Perturbation around energy level s

Example 4.1: Slow nucleus passing an atom

$$H'(t) = -\boldsymbol{\mu} \cdot \mathbf{E}(t) \tag{4.100}$$

with

$$H'_{ms} = -\boldsymbol{\mu}_{ms} \cdot \mathbf{E}(t), \tag{4.101}$$

where

$$\boldsymbol{\mu}_{ms} = \left\langle \psi_m^{(0)} \middle| \boldsymbol{\mu} \middle| \psi_s^{(0)} \right\rangle. \tag{4.102}$$

Using our previous nucleus passing an atom example, as depicted in fig. 4.4

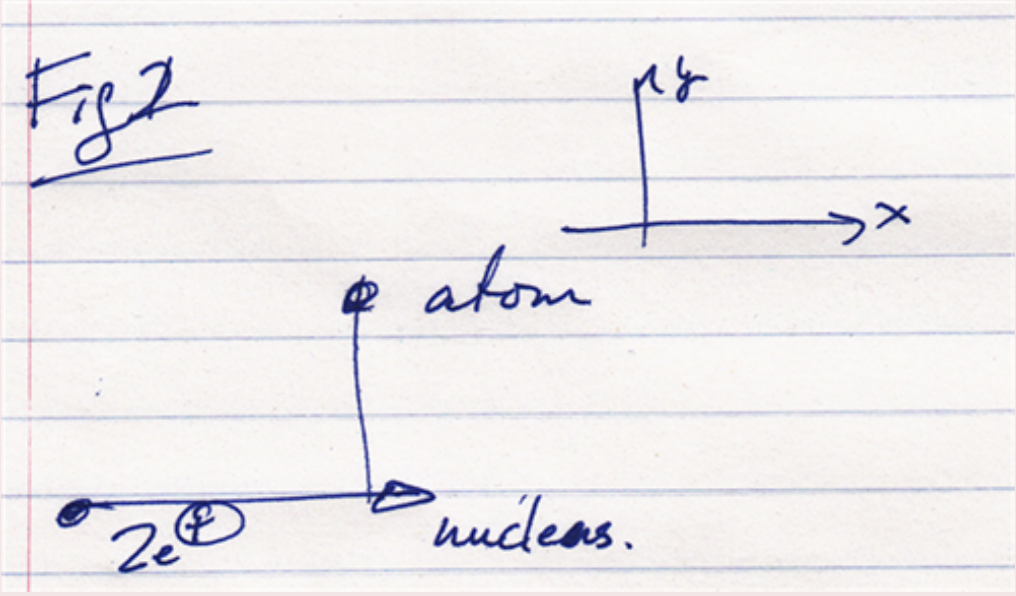

Figure 4.4: Slow nucleus passing an atom

We have

$$\boldsymbol{\mu} = \sum_i q_i \mathbf{R}_i, \tag{4.103}$$

the dipole moment for each of the charges in the atom. We will have fields as depicted in fig. 4.5

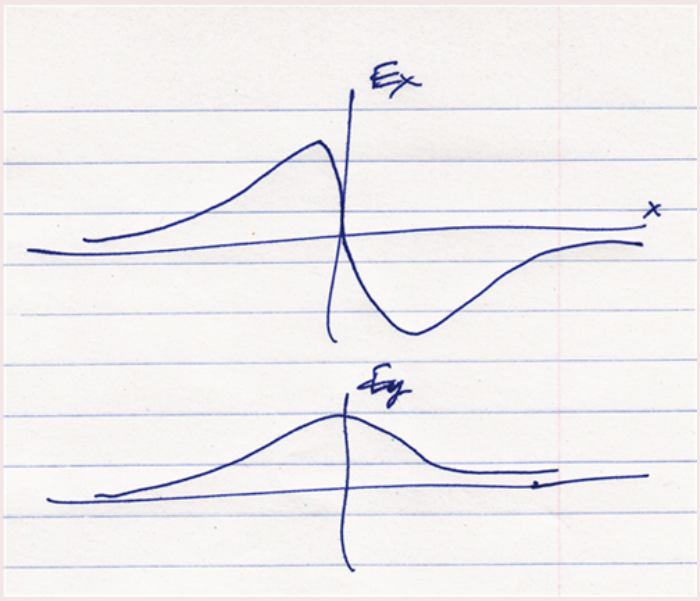

Figure 4.5: Fields for nucleus atom example

FIXME: think through.

Example 4.2: Electromagnetic wave pulse interacting with an atom

Consider a EM wave pulse, perhaps Gaussian, of the form depicted in fig. 4.6

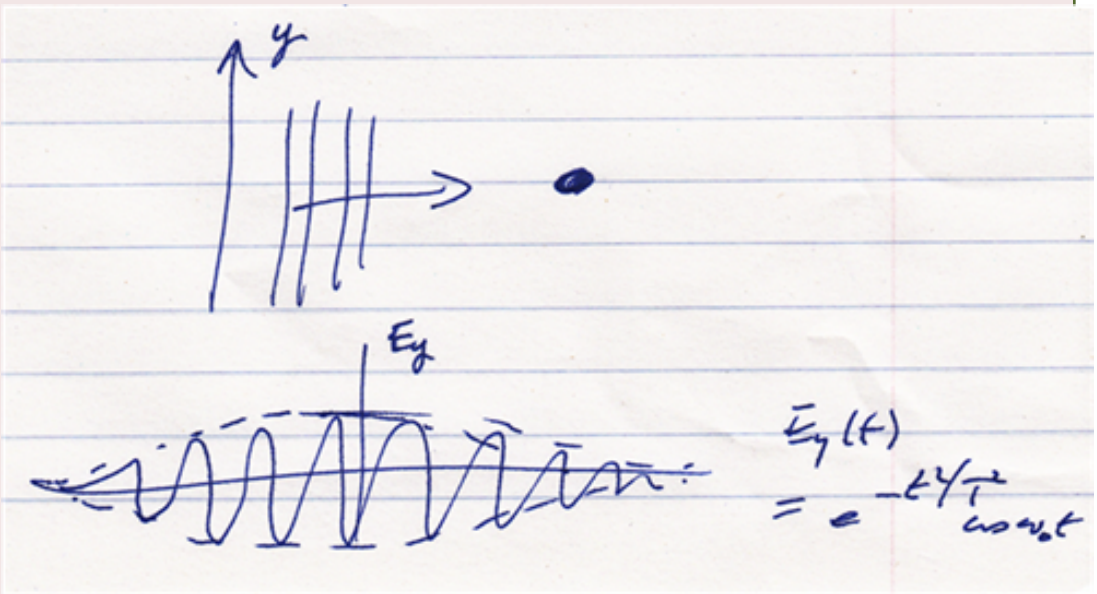

Figure 4.6: Atom interacting with an EM pulse

$$E_y(t) = e^{-t^2/T^2} \cos(\omega_0 t). \tag{4.104}$$

As we learned very early, perhaps sitting on our mother's knee, we can solve the differential equation eq. (4.99) for the first order perturbation, by direct integration

$$c_m^{(1)}(t) = \frac{1}{i\hbar} \int_{-\infty}^{t} H'_{ms}(t') e^{i\omega_{ms}t'} dt'. \tag{4.105}$$

Here the perturbation is assumed equal to zero at $-\infty$. Suppose our electric field is specified in terms of a Fourier transform

$$\mathbf{E}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \mathbf{E}(\omega) e^{-i\omega t}, \tag{4.106}$$

so

$$c_m^{(1)}(t) = \frac{\boldsymbol{\mu}_{ms}}{2\pi i\hbar} \cdot \int_{-\infty}^{\infty}\int_{-\infty}^{t} \mathbf{E}(\omega) e^{i(\omega_{ms}-\omega)t'} dt' d\omega. \tag{4.107}$$

From this, "after the perturbation", as $t \to \infty$ we find

$$\begin{aligned} c_m^{(1)}(\infty) &= \frac{\boldsymbol{\mu}_{ms}}{2\pi i\hbar} \cdot \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathbf{E}(\omega) e^{i(\omega_{ms}-\omega)t'} dt' d\omega \\ &= \frac{\boldsymbol{\mu}_{ms}}{i\hbar} \cdot \int_{-\infty}^{\infty} \mathbf{E}(\omega)\delta(\omega_{ms}-\omega) d\omega \end{aligned} \tag{4.108}$$

since we identify

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i(\omega_{ms}-\omega)t'} dt' \equiv \delta(\omega_{ms}-\omega) \tag{4.109}$$

Thus the steady state first order perturbation coefficient is

$$c_m^{(1)}(\infty) = \frac{\boldsymbol{\mu}_{ms}}{i\hbar} \cdot \mathbf{E}(\omega_{ms}). \tag{4.110}$$

Frequency symmetry for the Fourier spectrum of a real field We will look further at this next week, but we first require an intermediate result from transform theory. Because our field is real, we have

$$\mathbf{E}^*(t) = \mathbf{E}(t) \tag{4.111}$$

so

$$\begin{aligned} \mathbf{E}^*(t) &= \int \frac{d\omega}{2\pi} \mathbf{E}^*(\omega) e^{i\omega t} \\ &= \int \frac{d\omega}{2\pi} \mathbf{E}^*(-\omega) e^{-i\omega t} \end{aligned} \tag{4.112}$$

and thus

$$\mathbf{E}(\omega) = \mathbf{E}^*(-\omega), \tag{4.113}$$

and

$$|\mathbf{E}(\omega)|^2 = |\mathbf{E}(-\omega)|^2. \tag{4.114}$$

We will see shortly what the point of this aside is.

4.7 TIME DEPENDENT PERTURBATION

We would gotten as far as calculating

$$c_m^{(1)}(\infty) = \frac{1}{i\hbar}\boldsymbol{\mu}_{ms} \cdot \mathbf{E}(\omega_{ms}) \tag{4.115}$$

where

$$\mathbf{E}(t) = \int \frac{d\omega}{2\pi}\mathbf{E}(\omega)e^{-i\omega t}, \tag{4.116}$$

and

$$\omega_{ms} = \frac{E_m - E_s}{\hbar}. \tag{4.117}$$

Graphically, these frequencies are illustrated in fig. 4.7
The probability for a transition from m to s is therefore

$$\rho_{m\to s} = \left|c_m^{(1)}(\infty)\right|^2 = \frac{1}{\hbar}^2 \left|\boldsymbol{\mu}_{ms} \cdot \mathbf{E}(\omega_{ms})\right|^2 \tag{4.118}$$

Recall that because the electric field is real we had

$$|\mathbf{E}(\omega)|^2 = |\mathbf{E}(-\omega)|^2. \tag{4.119}$$

Suppose that we have a wave pulse, where our field magnitude is perhaps of the form

$$E(t) = e^{-t^2/T^2}\cos(\omega_0 t), \tag{4.120}$$

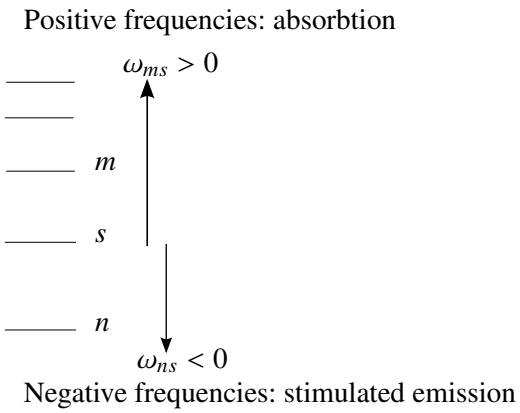

Figure 4.7: Positive and negative frequencies

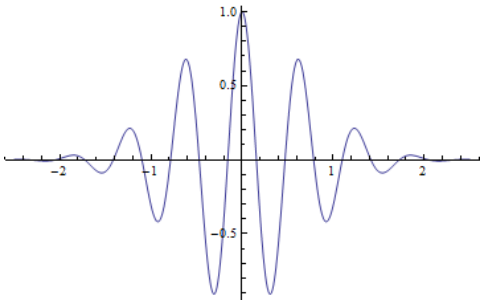

Figure 4.8: Gaussian wave packet

as illustrated with $\omega = 10, T = 1$ in fig. 4.8.

We expect this to have a two lobe Fourier spectrum, with the lobes centered at $\omega = \pm 10$, and width proportional to $1/T$.

For reference, as calculated using qmTwoL8figures.nb this Fourier transform is

$$E(\omega) = \frac{e^{-\frac{1}{4}T^2(\omega_0+\omega)^2}}{2\sqrt{\frac{2}{T^2}}} + \frac{e^{\omega_0 T^2\omega - \frac{1}{4}T^2(\omega_0+\omega)^2}}{2\sqrt{\frac{2}{T^2}}} \tag{4.121}$$

This is illustrated, again for $\omega_0 = 10$, and $T = 1$, in fig. 4.9

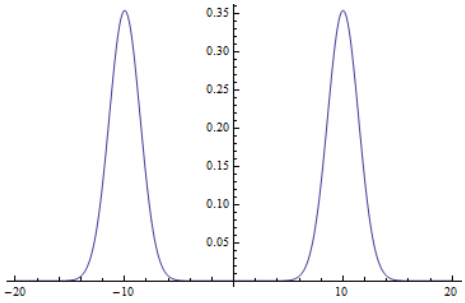

Figure 4.9: FTgaussianWavePacket

where we see the expected Gaussian result, since the Fourier transform of a Gaussian is a Gaussian.

FIXME: not sure what the point of this was?

4.8 SUDDEN PERTURBATIONS

Given our wave equation

$$i\hbar\frac{d}{dt}|\psi(t)\rangle = H(t)|\psi(t)\rangle \tag{4.122}$$

and a sudden perturbation in the Hamiltonian, as illustrated in fig. 4.10

Consider H_0 and H_F fixed, and decrease $\Delta t \to 0$. We can formally integrate eq. (4.122)

$$\frac{d}{dt}|\psi(t)\rangle = \frac{1}{i\hbar}H(t)|\psi(t)\rangle \tag{4.123}$$

For

$$|\psi(t)\rangle - |\psi(t_0)\rangle = \frac{1}{i\hbar}\int_{t_0}^{t} H(t')\left|\psi(t')\right\rangle dt'. \tag{4.124}$$

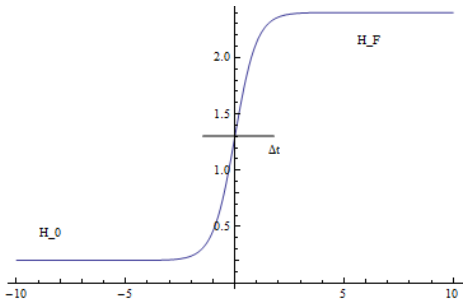

Figure 4.10: Sudden step Hamiltonian

While this is an exact solution, it is also not terribly useful since we do not know $|\psi(t)\rangle$. However, we can select the small interval Δt, and write

$$|\psi(\Delta t/2)\rangle = |\psi(-\Delta t/2)\rangle + \frac{1}{i\hbar}\int_{t_0}^{t} H(t')\,|\psi(t')\rangle\,dt'. \tag{4.125}$$

Note that we could use the integral kernel iteration technique here and substitute $|\psi(t')\rangle = |\psi(-\Delta t/2)\rangle$ and then develop this, to generate a power series with $(\Delta t/2)^k$ dependence. However, we note that eq. (4.125) is still an exact relation, and if $\Delta t \to 0$, with the integration limits narrowing (provided $H(t')$ is well behaved) we are left with just

$$|\psi(\Delta t/2)\rangle = |\psi(-\Delta t/2)\rangle \tag{4.126}$$

Or

$$|\psi_{\text{after}}\rangle = |\psi_{\text{before}}\rangle\,, \tag{4.127}$$

provided that we change the Hamiltonian fast enough. On the surface there appears to be no consequences, but there are some very serious ones!

Example 4.3: Harmonic oscillator

Consider our harmonic oscillator Hamiltonian, with

$$\begin{aligned} H_0 &= \frac{P^2}{2m} + \frac{1}{2}m\omega_0^2 X^2 \\ H_F &= \frac{P^2}{2m} + \frac{1}{2}m\omega_F^2 X^2 \end{aligned} \tag{4.128}$$

Here $\omega_0 \to \omega_F$ continuously, but very quickly. In effect, we have tightened the spring constant. Note that there are cases in linear optics when you can actually do exactly that.

Imagine that $|\psi_{\text{before}}\rangle$ is in the ground state of the harmonic oscillator as in fig. 4.11

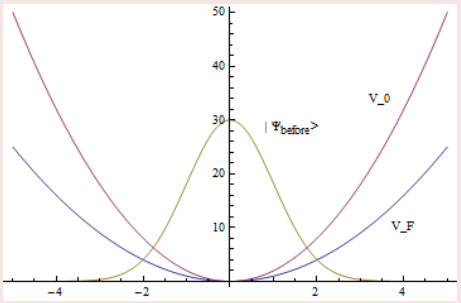

Figure 4.11: Harmonic oscillator sudden Hamiltonian perturbation

and we suddenly change the Hamiltonian with potential $V_0 \to V_F$ (weakening the "spring"). Professor Sipe gives us a graphical demo of this, by impersonating a constrained wavefunction with his arms, doing weak chicken-flapping of them. Now with the potential weakened, he wiggles and flaps his arms with more freedom and somewhat chaotically. His "wave function" arms are now bouncing around in the new limiting potential (initially over doing it and then bouncing back).

We had in this case the exact relation

$$H_0 \left|\psi_0^{(0)}\right\rangle = \frac{1}{2}\hbar\omega_0 \left|\psi_0^{(0)}\right\rangle \tag{4.129}$$

but we also have

$$|\psi_{\text{after}}\rangle = |\psi_{\text{before}}\rangle = \left|\psi_0^{(0)}\right\rangle \tag{4.130}$$

and

$$H_F \left|\psi_n^{(f)}\right\rangle = \frac{1}{2}\hbar\omega_F \left(n + \frac{1}{2}\right)\left|\psi_n^{(f)}\right\rangle \tag{4.131}$$

So

$$
\begin{aligned}
|\psi_{\text{after}}\rangle &= \left|\psi_0^{(0)}\right\rangle \\
&= \sum_n \left|\psi_n^{(f)}\right\rangle \overbrace{\left\langle\psi_n^{(f)}\middle|\psi_0^{(0)}\right\rangle}^{c_n} \\
&= \sum_n c_n \left|\psi_n^{(f)}\right\rangle
\end{aligned}
\tag{4.132}
$$

and at later times

$$
\begin{aligned}
\left|\psi(t)^{(f)}\right\rangle &= \left|\psi_0^{(0)}\right\rangle \\
&= \sum_n c_n e^{i\omega_n^{(f)} t} \left|\psi_n^{(f)}\right\rangle,
\end{aligned}
\tag{4.133}
$$

whereas

$$
\left|\psi(t)^{(o)}\right\rangle = e^{i\omega_0^{(0)} t} \left|\psi_0^{(0)}\right\rangle,
\tag{4.134}
$$

So, while the wave functions may be exactly the same after such a sudden change in Hamiltonian, the dynamics of the situation change for all future times, since we now have a wavefunction that has a different set of components in the basis for the new Hamiltonian. In particular, the evolution of the wave function is now significantly more complex.

FIXME: plot an example of this.

4.9 ADIABATIC PERTURBATIONS

This is treated in §17.5.2 of the text [4].

I wondered what Adiabatic meant in this context. The usage in class sounds like it was just "really slow and gradual", yet this has a definition "Of, relating to, or being a reversible thermodynamic process that occurs without gain or loss of heat and without a change in entropy". Wikipedia [14] appears to confirm that the QM meaning of this term is just "slow" changing.

This is the reverse case, and we now vary the Hamiltonian $H(t)$ very slowly.

$$
\frac{d}{dt}|\psi(t)\rangle = \frac{1}{i\hbar} H(t)|\psi(t)\rangle
\tag{4.135}
$$

We first consider only non-degenerate states, and at $t = 0$ write

$$H(0) = H_0, \tag{4.136}$$

and

$$H_0 \left|\psi_s^{(0)}\right\rangle = E_s^{(0)} \left|\psi_s^{(0)}\right\rangle \tag{4.137}$$

Imagine that at each time t we can find the "instantaneous" energy eigenstates

$$H(t) \left|\hat{\psi}_s(t)\right\rangle = E_s(t) \left|\hat{\psi}_s(t)\right\rangle \tag{4.138}$$

These states do not satisfy Schrödinger's equation, but are simply solutions to the eigen problem. Our standard strategy in perturbation is based on analysis of

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-i\omega_n^{(0)} t} \left|\psi_n^{(0)}\right\rangle, \tag{4.139}$$

Here instead

$$|\psi(t)\rangle = \sum_n b_n(t) \left|\hat{\psi}_n(t)\right\rangle, \tag{4.140}$$

we will expand, not using our initial basis, but instead using the instantaneous kets. Plugging into Schrödinger's equation we have

$$\begin{aligned} H(t) |\psi(t)\rangle &= H(t) \sum_n b_n(t) \left|\hat{\psi}_n(t)\right\rangle \\ &= \sum_n b_n(t) E_n(t) \left|\hat{\psi}_n(t)\right\rangle \end{aligned} \tag{4.141}$$

This was complicated before with matrix elements all over the place. Now it is easy, however, the time derivative becomes harder. Doing that we find

$$\begin{aligned} i\hbar \frac{d}{dt} |\psi(t)\rangle &= i\hbar \frac{d}{dt} \sum_n b_n(t) \left|\hat{\psi}_n(t)\right\rangle \\ &= i\hbar \sum_n \frac{db_n(t)}{dt} \left|\hat{\psi}_n(t)\right\rangle + \sum_n b_n(t) \frac{d}{dt} \left|\hat{\psi}_n(t)\right\rangle \\ &= \sum_n b_n(t) E_n(t) \left|\hat{\psi}_n(t)\right\rangle \end{aligned} \tag{4.142}$$

We bra $\left\langle \hat{\psi}_m(t) \right|$ into this

$$i\hbar \sum_n \frac{db_n(t)}{dt} \left\langle \hat{\psi}_m(t) \middle| \hat{\psi}_n(t) \right\rangle + \sum_n b_n(t) \left\langle \hat{\psi}_m(t) \right| \frac{d}{dt} \left| \hat{\psi}_n(t) \right\rangle = \sum_n b_n(t) E_n(t) \left\langle \hat{\psi}_m(t) \middle| \hat{\psi}_n(t) \right\rangle, \quad (4.143)$$

and find

$$i\hbar \frac{db_m(t)}{dt} + \sum_n b_n(t) \left\langle \hat{\psi}_m(t) \right| \frac{d}{dt} \left| \hat{\psi}_n(t) \right\rangle = b_m(t) E_m(t) \quad (4.144)$$

If the Hamiltonian is changed very very slowly in time, we can imagine that $\left| \hat{\psi}_n(t) \right\rangle'$ is also changing very very slowly, but we are not quite there yet. Let us first split our sum of bra and ket products

$$\sum_n b_n(t) \left\langle \hat{\psi}_m(t) \right| \frac{d}{dt} \left| \hat{\psi}_n(t) \right\rangle \quad (4.145)$$

into $n \neq m$ and $n = m$ terms. Looking at just the $n = m$ term

$$\left\langle \hat{\psi}_m(t) \right| \frac{d}{dt} \left| \hat{\psi}_m(t) \right\rangle \quad (4.146)$$

we note

$$\begin{aligned} 0 &= \frac{d}{dt} \left\langle \hat{\psi}_m(t) \middle| \hat{\psi}_m(t) \right\rangle \\ &= \left(\frac{d}{dt} \left\langle \hat{\psi}_m(t) \right| \right) \left| \hat{\psi}_m(t) \right\rangle + \left\langle \hat{\psi}_m(t) \right| \frac{d}{dt} \left| \hat{\psi}_m(t) \right\rangle \end{aligned} \quad (4.147)$$

Something plus its complex conjugate equals 0

$$a + ib + (a + ib)^* = 2a = 0 \implies a = 0, \quad (4.148)$$

so $\left\langle \hat{\psi}_m(t) \right| \frac{d}{dt} \left| \hat{\psi}_m(t) \right\rangle$ must be purely imaginary. We write

$$\left\langle \hat{\psi}_m(t) \right| \frac{d}{dt} \left| \hat{\psi}_m(t) \right\rangle = -i\Gamma_s(t), \quad (4.149)$$

where Γ_s is real.

4.10 ADIABATIC PERTURBATION THEORY (CONT.)

We were working through Adiabatic time dependent perturbation (as also covered in §17.5.2 of the text [4].)

Utilizing an expansion

$$\begin{aligned}|\psi(t)\rangle &= \sum_n c_n(t) e^{-i\omega_n^{(0)} t} \left|\psi_n^{(0)}\right\rangle \\ &= \sum_n b_n(t) \left|\hat{\psi}_n(t)\right\rangle,\end{aligned} \tag{4.150}$$

where

$$H(t)\left|\hat{\psi}_s(t)\right\rangle = E_s(t)\left|\hat{\psi}_s(t)\right\rangle \tag{4.151}$$

and found

$$\frac{db_s(t)}{dt} = -i\left(\omega_s(t) - \Gamma_s(t)\right) b_s(t) - \sum_{n\neq s} b_n(t)\left\langle\hat{\psi}_s(t)\right| \frac{d}{dt}\left|\hat{\psi}_n(t)\right\rangle \tag{4.152}$$

where

$$\Gamma_s(t) = i\left\langle\hat{\psi}_s(t)\right| \frac{d}{dt}\left|\hat{\psi}_s(t)\right\rangle \tag{4.153}$$

Look for a solution of the form

$$\begin{aligned}b_s(t) &= \bar{b}_s(t) e^{-i\int_0^t dt'(\omega_s(t') - \Gamma_s(t'))} \\ &= \bar{b}_s(t) e^{-i\gamma_s(t)}\end{aligned} \tag{4.154}$$

where

$$\gamma_s(t) = \int_0^t dt'(\omega_s(t') - \Gamma_s(t')). \tag{4.155}$$

Taking derivatives of $\bar{b}_s$ and after a bit of manipulation we find that things conveniently cancel

$$\begin{aligned}\frac{d\bar{b}_s(t)}{dt} &= \frac{d}{dt}\left(b_s(t) e^{i\gamma_s(t)}\right) \\ &= \frac{db_s(t)}{dt} e^{i\gamma_s(t)} + b_s(t)\frac{d}{dt} e^{i\gamma_s(t)} \\ &= \frac{db_s(t)}{dt} e^{i\gamma_s(t)} + b_s(t) i(\omega_s(t) - \Gamma_s(t)) e^{i\gamma_s(t)}.\end{aligned} \tag{4.156}$$

We find

$$\begin{aligned}\frac{d\bar{b}_s(t)}{dt}e^{-i\gamma_s(t)} &= \frac{db_s(t)}{dt} + ib_s(t)(\omega_s(t) - \Gamma_s(t)) \\ &= \cancel{ib_s(t)(\omega_s(t) - \Gamma_s(t))} - \cancel{i\left(\omega_s(t) - \Gamma_s(t)\right)b_s(t)} - \sum_{n\neq s} b_n(t)\left\langle\hat{\psi}_s(t)\right| \frac{d}{dt}\left|\hat{\psi}_n(t)\right\rangle,\end{aligned} \tag{4.157}$$

so

$$\begin{aligned}\frac{d\bar{b}_s(t)}{dt} &= -\sum_{n\neq s} b_n(t)e^{i\gamma_s(t)}\left\langle\hat{\psi}_s(t)\right| \frac{d}{dt}\left|\hat{\psi}_n(t)\right\rangle \\ &= -\sum_{n\neq s} \bar{b}_n(t)e^{i(\gamma_s(t)-\gamma_n(t))}\left\langle\hat{\psi}_s(t)\right| \frac{d}{dt}\left|\hat{\psi}_n(t)\right\rangle.\end{aligned} \tag{4.158}$$

With a last bit of notation

$$\gamma_{sn}(t) = \gamma_s(t) - \gamma_n(t)), \tag{4.159}$$

the problem is reduced to one involving only the sums over the $n \neq s$ terms, and where all the dependence on $\left\langle\hat{\psi}_s(t)\right| \frac{d}{dt}\left|\hat{\psi}_s(t)\right\rangle$ has been nicely isolated in a phase term

$$\frac{d\bar{b}_s(t)}{dt} = -\sum_{n\neq s} \bar{b}_n(t)e^{i\gamma_{sn}(t)}\left\langle\hat{\psi}_s(t)\right| \frac{d}{dt}\left|\hat{\psi}_n(t)\right\rangle. \tag{4.160}$$

Looking for an approximate solution

Try : An approximate solution

$$\bar{b}_n(t) = \delta_{nm} \tag{4.161}$$

For $s = m$ this is okay, since we have $\frac{d\delta_{ns}}{dt} = 0$ which is consistent with

$$\sum_{n\neq s} \delta_{ns}(\cdots) = 0 \tag{4.162}$$

However, for $s \neq m$ we get

$$\begin{aligned}\frac{d\bar{b}_s(t)}{dt} &= -\sum_{n\neq s} \delta_{nm} e^{i\gamma_{sn}(t)} \left\langle \hat{\psi}_s(t) \right| \frac{d}{dt} \left| \hat{\psi}_n(t) \right\rangle \\ &= -e^{i\gamma_{sm}(t)} \left\langle \hat{\psi}_s(t) \right| \frac{d}{dt} \left| \hat{\psi}_m(t) \right\rangle\end{aligned} \tag{4.163}$$

But

$$\gamma_{sm}(t) = \int_0^t dt' \left(\frac{1}{\hbar}(E_s(t') - E_m(t')) - \Gamma_s(t') + \Gamma_m(t') \right) \tag{4.164}$$

FIXME: I think we argued in class that the Γ contributions are negligible. Why was that? Now, are energy levels will have variation with time, as illustrated in fig. 4.12

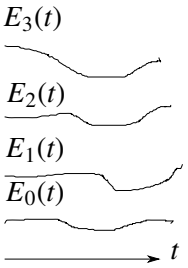

Figure 4.12: Energy level variation with time

Perhaps unrealistically, suppose that our energy levels have some "typical" energy difference ΔE, so that

$$\gamma_{sm}(t) \approx \frac{\Delta E}{\hbar} t \equiv \frac{t}{\tau}, \tag{4.165}$$

or

$$\tau = \frac{\hbar}{\Delta E} \tag{4.166}$$

Suppose that τ is much less than a typical time T over which instantaneous quantities (wavefunctions and brakets) change. After a large time T

$$e^{i\gamma_{sm}(t)} \approx e^{iT/\tau} \tag{4.167}$$

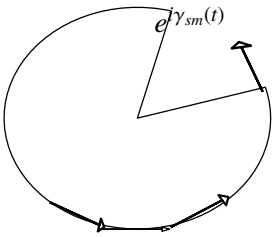

Figure 4.13: Phase whipping around

so we have our phase term whipping around really fast, as illustrated in fig. 4.13.

So, while $\left\langle \hat{\psi}_s(t) \right| \frac{d}{dt} \left| \hat{\psi}_m(t) \right\rangle$ is moving really slow, but our phase space portion is changing really fast. The key to the approximate solution is factoring out this quickly changing phase term.

Note $\Gamma_s(t)$ is called the "Berry" phase [15], whereas the $E_s(t')/\hbar$ part is called the geometric phase, and can be shown to have a geometric interpretation.

To proceed we can introduce λ terms, perhaps

$$\bar{b}_s(t) = \delta_{ms} + \lambda \bar{b}_s^{(1)}(t) + \cdots \tag{4.168}$$

and

$$-\sum_{n \neq s} e^{i\gamma_{sn}(t)} \lambda(\cdots) \tag{4.169}$$

This λ approximation and a similar Taylor series expansion in time have been explored further in 19.

Degeneracy Suppose we have some branching of energy levels that were initially degenerate, as illustrated in fig. 4.14

We have a necessity to choose states properly so there is a continuous evolution in the instantaneous eigenvalues as $H(t)$ changes.

Question: A physical example? FIXME: Prof Sipe to ponder and revisit.

4.11 EXAMPLES

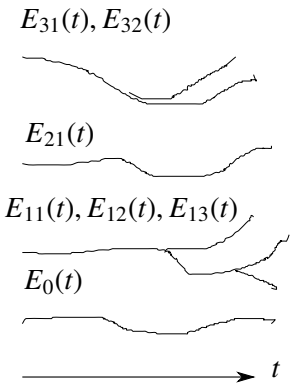

Figure 4.14: Degenerate energy level splitting

Example 4.4: Adiabatic perturbation theory

Utilizing instantaneous eigenstates

$$|\psi(t)\rangle = \sum_\alpha b_\alpha(t) \left|\hat{\psi}_\alpha(t)\right\rangle \tag{4.170}$$

where

$$H(t) \left|\hat{\psi}_\alpha(t)\right\rangle = E_\alpha(t) \left|\hat{\psi}_\alpha(t)\right\rangle \tag{4.171}$$

We found

$$b_\alpha(t) = \bar{b}_\alpha(t) e^{-\frac{i}{\hbar}\int_0^t (E_\alpha(t') - \hbar\Gamma_\alpha(t'))dt'} \tag{4.172}$$

where

$$\Gamma_\alpha = i \left\langle \hat{\psi}_\alpha(t) \right| \frac{d}{dt} \left|\hat{\psi}_\alpha(t)\right\rangle \tag{4.173}$$

and

$$\frac{d}{dt}\bar{b}_\alpha(t) = -\sum_{\beta\neq\alpha}\bar{b}_\beta(t)e^{-\frac{i}{\hbar}\int_0^t(E_{\beta\alpha}(t')-\hbar\Gamma_{\beta\alpha}(t'))dt'}\left\langle\hat{\psi}_\alpha(t)\right|\frac{d}{dt}\left|\hat{\psi}_\beta(t)\right\rangle \tag{4.174}$$

Suppose we start in a subspace

$$\text{span}\left\{\frac{1}{\sqrt{2}}(|2,0,0\rangle \pm |2,1,0\rangle), |2,1,\pm 1\rangle\right\} \tag{4.175}$$

Now expand the bra derivative kets

$$\left\langle\hat{\psi}_\alpha(t)\right|\frac{d}{dt}\left|\hat{\psi}_\beta(t)\right\rangle = \left(\left\langle\psi_\alpha^{(0)}\right| + \sum_\gamma \frac{\left\langle\psi_\gamma^{(0)}\right|H'\left|\psi_\alpha^{(0)}\right\rangle\left\langle\psi_\gamma^{(0)}\right|}{E_\alpha^{(0)}-E_\gamma^{(0)}}\right)\frac{d}{dt}\left(\left|\psi_\beta^{(0)}\right\rangle + \sum_{\gamma'}\frac{\left|\psi_{\gamma'}^{(0)}\right\rangle\left\langle\psi_{\gamma'}^{(0)}\right|H'\left|\psi_\beta^{(0)}\right\rangle}{E_\beta^{(0)}-E_{\gamma'}^{(0)}}\right) \tag{4.176}$$

To first order we can drop the quadratic terms in γ, γ' leaving

$$\left\langle\hat{\psi}_\alpha(t)\right|\frac{d}{dt}\left|\hat{\psi}_\beta(t)\right\rangle \sim \sum_{\gamma'}\left\langle\psi_\alpha^{(0)}\middle|\psi_{\gamma'}^{(0)}\right\rangle\frac{\left\langle\psi_{\gamma'}^{(0)}\right|\frac{dH'(t)}{dt}\left|\psi_\beta^{(0)}\right\rangle}{E_\beta^{(0)}-E_{\gamma'}^{(0)}} = \frac{\left\langle\psi_\alpha^{(0)}\right|\frac{dH'(t)}{dt}\left|\psi_\beta^{(0)}\right\rangle}{E_\beta^{(0)}-E_\alpha^{(0)}} \tag{4.177}$$

so

$$\frac{d}{dt}\bar{b}_\alpha(t) = -\sum_{\beta\neq\alpha}\bar{b}_\beta(t)e^{-\frac{i}{\hbar}\int_0^t(E_{\beta\alpha}(t')-\hbar\Gamma_{\beta\alpha}(t'))dt'}\frac{\left\langle\psi_\alpha^{(0)}\right|\frac{dH'(t)}{dt}\left|\psi_\beta^{(0)}\right\rangle}{E_\beta^{(0)}-E_\alpha^{(0)}} \tag{4.178}$$

A different way to this end result A result of this form is also derived in [2] §20.1, but with a different approach. There he takes derivatives of

$$H(t)\left|\hat{\psi}_\beta(t)\right\rangle = E_\beta(t)\left|\hat{\psi}_\beta(t)\right\rangle, \tag{4.179}$$

$$\frac{dH(t)}{dt}\left|\hat{\psi}_\beta(t)\right\rangle + H(t)\frac{d}{dt}\left|\hat{\psi}_\beta(t)\right\rangle = \frac{dE_\beta(t)}{dt}\left|\hat{\psi}_\beta(t)\right\rangle + E_\beta(t)\frac{d}{dt}\left|\hat{\psi}_\beta(t)\right\rangle \tag{4.180}$$

Bra'ing $\left\langle\hat{\psi}_\alpha(t)\right|$ into this we have, for $\alpha \neq \beta$

$$\left\langle\hat{\psi}_\alpha(t)\right|\frac{dH(t)}{dt}\left|\hat{\psi}_\beta(t)\right\rangle + \left\langle\hat{\psi}_\alpha(t)\right|H(t)\frac{d}{dt}\left|\hat{\psi}_\beta(t)\right\rangle = \cancel{\left\langle\hat{\psi}_\alpha(t)\right|\frac{dE_\beta(t)}{dt}\left|\hat{\psi}_\beta(t)\right\rangle} + \left\langle\hat{\psi}_\alpha(t)\right|E_\beta(t)\frac{d}{dt}\left|\hat{\psi}_\beta(t)\right\rangle$$
$$\left\langle\hat{\psi}_\alpha(t)\right|\frac{dH(t)}{dt}\left|\hat{\psi}_\beta(t)\right\rangle + E_\alpha(t)\left\langle\hat{\psi}_\alpha(t)\right|\frac{d}{dt}\left|\hat{\psi}_\beta(t)\right\rangle = \tag{4.181}$$

or

$$\left\langle\hat{\psi}_\alpha(t)\right|\frac{d}{dt}\left|\hat{\psi}_\beta(t)\right\rangle = \frac{\left\langle\hat{\psi}_\alpha(t)\right|\frac{dH(t)}{dt}\left|\hat{\psi}_\beta(t)\right\rangle}{E_\beta(t) - E_\alpha(t)} \tag{4.182}$$

so without the implied λ perturbation of $\left|\hat{\psi}_\alpha(t)\right\rangle$ we can from eq. (4.174) write the exact generalization of eq. (4.178) as

$$\frac{d}{dt}\bar{b}_\alpha(t) = -\sum_{\beta\neq\alpha}\bar{b}_\beta(t)e^{-\frac{i}{\hbar}\int_0^t(E_{\beta\alpha}(t')-\hbar\Gamma_{\beta\alpha}(t'))dt'}\frac{\left\langle\hat{\psi}_\alpha(t)\right|\frac{dH(t)}{dt}\left|\hat{\psi}_\beta(t)\right\rangle}{E_\beta(t) - E_\alpha(t)} \tag{4.183}$$

5

FERMI'S GOLDEN RULE

See §17.2 of the text [4].

Fermi originally had two golden rules, but his first one has mostly been forgotten. This refers to his second.

This is really important, and probably the single most important thing to learn in this course. You will find this falls out of many complex calculations.

Returning to general time dependent equations with

$$H = H_0 + H'(t) \tag{5.1}$$

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-i\omega_n t} |\psi_n\rangle \tag{5.2}$$

and

$$i\hbar \dot{c}_n = \sum_n H'_{mn} e^{i\omega_{mn} t} c_n(t) \tag{5.3}$$

where

$$\begin{aligned} H'_{mn}(t) &= \langle \psi_m | H'(t) | \psi_n \rangle \\ \omega_n &= \frac{E_n}{\hbar} \\ \omega_{mn} &= \omega_m - \omega_n \end{aligned} \tag{5.4}$$

Example 5.1: Electric field potential

$$H'(t) = -\boldsymbol{\mu} \cdot \mathbf{E}(t). \tag{5.5}$$

If $c_m^{(0)} = \delta_{mi}$, then to first order

$$i\hbar \dot{c}^{(1)}(t) = H'_{mi}(t) e^{i\omega_{mi} t}, \tag{5.6}$$

and

$$c_m^{(1)}(t) = \frac{1}{i\hbar}\int_{t_0}^{t} H'_{mi}(t')e^{i\omega_{mi}t'}\,dt'. \tag{5.7}$$

Assume the perturbation vanishes before time t_0.

Reminder . Have considered this using eq. (5.7) for a pulse as in fig. 5.1

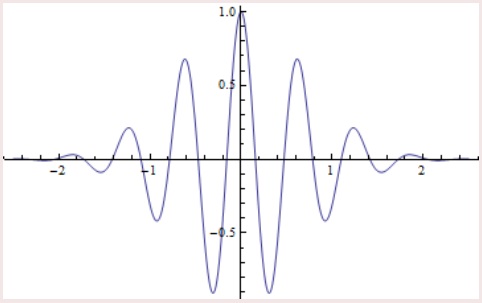

Figure 5.1: Gaussian wave packet

Now we want to consider instead a non-terminating signal, that was zero before some initial time as illustrated in fig. 5.2, where the separation between two peaks is $\Delta t = 2\pi/\omega_0$.

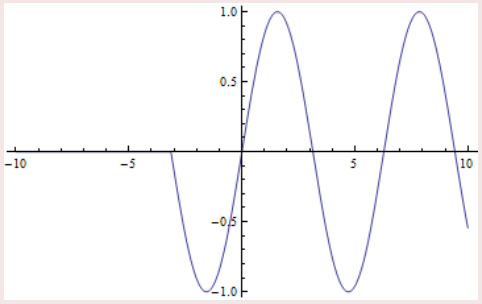

Figure 5.2: Sine only after an initial time

Our matrix element is

$$H'_{mi}(t) = -\langle\psi_m|\boldsymbol{\mu}|\psi_i\rangle\cdot\mathbf{E}(t) = \begin{cases} 2A_{mi}\sin(\omega_0 t) & \text{if } t > 0 \\ 0 & \text{if } t < 0 \end{cases} \tag{5.8}$$

Here the factor of 2 has been included for consistency with the text.

$$H'_{mi}(t) = iA_{mi}\left(e^{-i\omega_0 t} - e^{i\omega_0 t}\right) \tag{5.9}$$

Plug this into the perturbation

$$c_m^{(1)}(t) = \frac{A_{mi}}{\hbar}\int_{t_0}^{t} dt' \left(e^{i(\omega_{mi}-\omega_0 t)} - e^{i(\omega_{mi}+\omega_0 t)}\right) \tag{5.10}$$

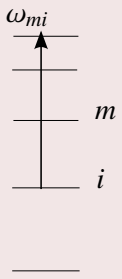

Figure 5.3: ω_{mi} illustrated

Suppose that

$$\omega_0 \approx \omega_{mi}, \tag{5.11}$$

then

$$c_m^{(1)}(t) \approx \frac{A_{mi}}{\hbar}\int_{t_0}^{t} dt' \left(1 - e^{2i\omega_0 t}\right), \tag{5.12}$$

but the exponential has essentially no contribution

$$\begin{aligned}\left|\int_0^t e^{2i\omega_0 t'}\,dt'\right| &= \left|\frac{e^{2i\omega_0 t}-1}{2i\omega_0}\right| \\ &= \frac{\sin(\omega_0 t)}{\omega_0} \\ &\sim \frac{1}{\omega_0}\end{aligned} \tag{5.13}$$

so for $t \gg \frac{1}{\omega_0}$ and $\omega_0 \approx \omega_{mi}$ we have

$$c_m^{(1)}(t) \approx \frac{A_{mi}}{\hbar} t \tag{5.14}$$

Similarly for $\omega_0 \approx \omega_{im}$ as in fig. 5.4

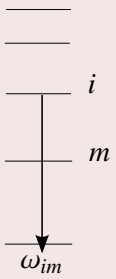

Figure 5.4: FIXME: qmTwoL9fig7

then

$$c_m^{(1)}(t) \approx \frac{A_{mi}}{\hbar}\int_{t_0}^t dt'\left(e^{-2i\omega_0 t}-1\right), \tag{5.15}$$

and we have

$$c_m^{(1)}(t) \approx -\frac{A_{mi}}{\hbar} t \tag{5.16}$$

5.1 RECAP. WHERE WE GOT TO ON FERMI'S GOLDEN RULE

We are continuing on the topic of Fermi golden rule, as also covered in §17.2 of the text [4]. Utilizing a wave train with peaks separation $\Delta t = 2\pi/\omega_0$, zero before some initial time fig. 5.5.

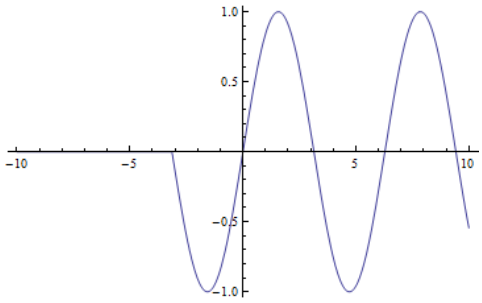

Figure 5.5: Sine only after an initial time

Perturbing a state in the ith energy level, and looking at the states for the mth energy level as illustrated in fig. 5.6

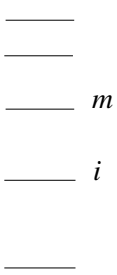

Figure 5.6: Perturbation from i to mth energy levels

Our matrix element was

$$\begin{aligned} H'_{mi}(t) &= 2A_m i \sin(\omega_0 t)\theta(t) \\ &= iA_{mi}(e^{-i\omega_0 t} - e^{i\omega_0 t})\theta(t), \end{aligned} \tag{5.17}$$

and we found

$$c_m^{(1)}(t) = \frac{A_{mi}}{\hbar}\int_0^t dt' \left(e^{i(\omega_{mi}-\omega_0)t'} - e^{i(\omega_{mi}+\omega_0)t'}\right), \tag{5.18}$$

and argued that

$$\left|c_m^{(1)}(t)\right|^2 \sim \left(\frac{A_{mi}}{\hbar}\right)^2 t^2 + \cdots \tag{5.19}$$

where $\omega_0 t \gg 1$ for $\omega_{mi} \sim \pm\omega_0$.
We can also just integrate eq. (5.18) directly

$$\begin{aligned} c_m^{(1)}(t) &= \frac{A_{mi}}{\hbar}\left(\frac{e^{i(\omega_{mi}-\omega_0)t}-1}{i(\omega_{mi}-\omega_0)} - \frac{e^{i(\omega_{mi}+\omega_0)t}-1}{i(\omega_{mi}+\omega_0)}\right) \\ &\equiv A_{mi}(\omega_0, t) - A_{mi}(-\omega_0, t), \end{aligned} \tag{5.20}$$

where

$$A_{mi}(\omega_0, t) = \frac{A_{mi}}{\hbar}\frac{e^{i(\omega_{mi}-\omega_0)t}-1}{i(\omega_{mi}-\omega_0)} \tag{5.21}$$

Factoring out the phase term, we have

$$A_{mi}(\omega_0, t) = \frac{2A_{mi}}{\hbar}e^{i(\omega_{mi}-\omega_0)t/2}\frac{\sin((\omega_{mi}-\omega_0)t/2)}{(\omega_{mi}-\omega_0)} \tag{5.22}$$

We we will have two lobes, centered on $\pm\omega_0$, as illustrated in fig. 5.7

5.2 FERMI'S GOLDEN RULE

Fermi's Golden rule applies to a continuum of states (there are other forms of Fermi's golden rule, but this is the one we will talk about, and is the one in the book). One example is the ionized

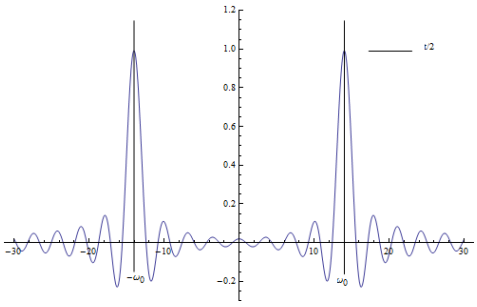

Figure 5.7: Two sinc lobes

Figure 5.8: Continuum of energy levels for ionized states of an atom

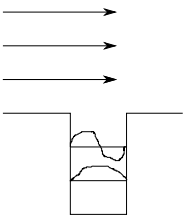

Figure 5.9: Semi-conductor well

states of an atom, where the energy level separation becomes so small that we can consider it continuous

Another example are the unbound states in a semiconductor well as illustrated in fig. 5.9

Note that we can have reflection from the well even in the continuum states where we would have no such reflection classically. However, with enough energy, states are approximately plane waves. In one dimension

$$\begin{aligned} \left\langle x \middle| \psi_p \right\rangle &\approx \frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}} \\ \left\langle \psi_p \middle| \psi'_p \right\rangle &= \delta(p - p') \end{aligned} \tag{5.23}$$

or in 3d

$$\begin{aligned} \left\langle \mathbf{r} \middle| \psi_{\mathbf{p}} \right\rangle &\approx \frac{e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}}{(2\pi\hbar)^{3/2}} \\ \left\langle \psi_{\mathbf{p}} \middle| \psi_{\mathbf{p}'} \right\rangle &= \delta^3(\mathbf{p} - \mathbf{p}') \end{aligned} \tag{5.24}$$

Let us consider the 1d model for the quantum well in more detail. Including both discrete and continuous states we have

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-i\omega_n t} |\psi_n\rangle + \int dp c_p(t) e^{-i\omega_p t} \left|\psi_p\right\rangle \tag{5.25}$$

Imagine at $t = 0$ that the wave function started in some discrete state, and look at the probability that we "kick the electron out of the well". Calculate

$$\mathcal{P} = \int dp \left| c_p^{(1)}(t) \right|^2 \tag{5.26}$$

Now, we assume that our matrix element has the following form

$$H'_{pi}(t) = \left(\bar{A}_{pi} e^{-i\omega_0 t} + \bar{B}_{pi} e^{i\omega_0 t} \right) \theta(t) \tag{5.27}$$

generalizing the wave train matrix element that we had previously

$$H'_{mi}(t) = iA_{mi} \left(e^{-i\omega_0 t} - e^{i\omega_0 t} \right) \theta(t) \tag{5.28}$$

Doing the perturbation we have

$$\mathcal{P} = \int dp \left| A_{pi}(\omega_0, t) + B_{pi}(-\omega_0, t) \right|^2 \tag{5.29}$$

where

$$A_{pi}(\omega_0, t) = \frac{2\bar{A}_{pi}}{i\hbar} e^{i(\omega_{pi}-\omega_0)t/2} \frac{\sin((\omega_{pi}-\omega_0)t/2)}{\omega_{pi}-\omega_0} \tag{5.30}$$

which is peaked at $\omega_{pi} = \omega_0$, and

$$B_{pi}(\omega_0, t) = \frac{2\bar{B}_{pi}}{i\hbar} e^{i(\omega_{pi}+\omega_0)t/2} \frac{\sin((\omega_{pi}+\omega_0)t/2)}{\omega_{pi}+\omega_0} \tag{5.31}$$

which is peaked at $\omega_{pi} = -\omega_0$.

FIXME: show that this is the perturbation result.

In eq. (5.29) at $t \gg 0$ the only significant contribution is from the A portion as illustrated in fig. 5.10 where we are down in the wiggles of A_{pi}.

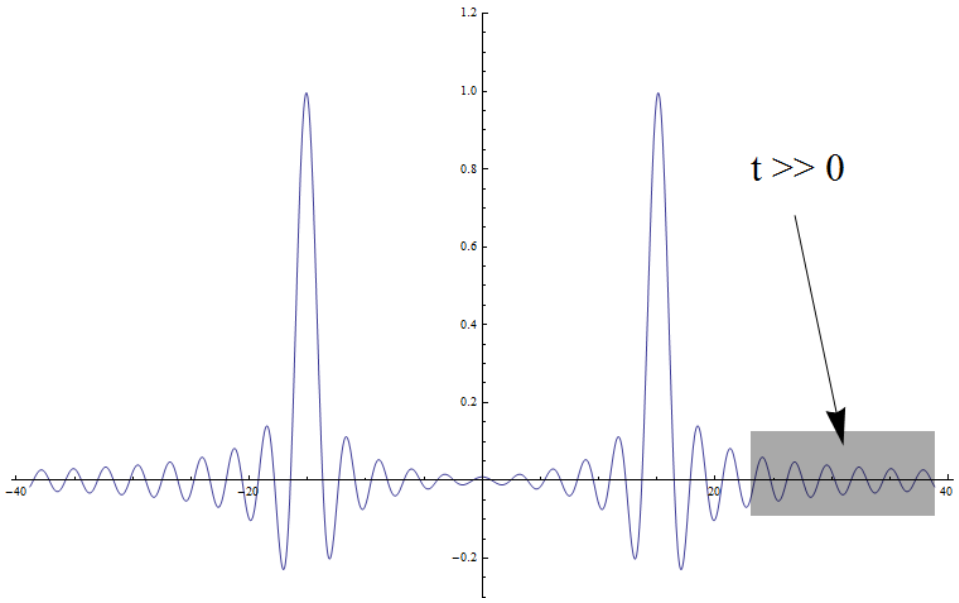

Figure 5.10

Our probability to find the particle in the continuum range is now approximately

$$\mathcal{P} = \int dp \left| A_{pi}(\omega_0, t) \right|^2 \tag{5.32}$$

With

$$\omega_{pi} - \omega_0 = \frac{1}{\hbar}\left(\frac{p^2}{2m} - E_i\right) - \omega_0, \tag{5.33}$$

define $\bar{p}$ so that

$$0 = \frac{1}{\hbar}\left(\frac{\bar{p}^2}{2m} - E_i\right) - \omega_0. \tag{5.34}$$

In momentum space, we know have the sinc functions peaked at $\pm\bar{p}$ as in fig. 5.11

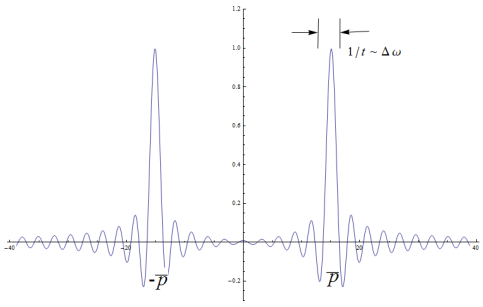

Figure 5.11: Momentum space view

The probability that the electron goes to the right is then

$$\begin{aligned} \mathcal{P}_+ &= \int_0^\infty dp \left| c_p^{(1)}(t) \right|^2 \\ &= \int_0^\infty dp \left| \bar{A}_{pi} \right|^2 \frac{\sin^2\left((\omega_{pi} - \omega_0)t/2\right)}{\left(\omega_{pi} - \omega_0\right)^2}, \end{aligned} \tag{5.35}$$

with

$$\omega_{pi} = \frac{1}{\hbar}\left(\frac{p^2}{2m} - E_i\right) \tag{5.36}$$

we have with a change of variables

$$\mathcal{P}_+ = \frac{4}{\hbar^2}\int_{-E_i/\hbar}^{\infty} d\omega_{pi}\left|\bar{A}_{pi}\right|^2 \frac{dp}{d\omega_{pi}}\frac{\sin^2\left((\omega_{pi}-\omega_0)t/2\right)}{\left(\omega_{pi}-\omega_0\right)^2}. \tag{5.37}$$

Now suppose we have t small enough so that $\mathcal{P}_+ \ll 1$ and t large enough so

$$\left|\bar{A}_{pi}\right|^2 \frac{dp}{d\omega_{pi}} \tag{5.38}$$

is roughly constant over $\Delta\omega$. This is a sort of "Goldilocks condition", a time that can not be too small, and can not be too large, but instead has to be "just right". Given such a condition

$$\mathcal{P}_+ = \frac{4}{\hbar^2}\left|\bar{A}_{pi}\right|^2 \frac{dp}{d\omega_{pi}}\int_{-E_i/\hbar}^{\infty} d\omega_{pi}\frac{\sin^2\left((\omega_{pi}-\omega_0)t/2\right)}{\left(\omega_{pi}-\omega_0\right)^2}, \tag{5.39}$$

where we can pull stuff out of the integral since the main contribution is at the peak. Provided $\bar{p}$ is large enough, using eq. (C.5), then

$$\begin{aligned}\int_{-E_i/\hbar}^{\infty} d\omega_{pi}\frac{\sin^2\left((\omega_{pi}-\omega_0)t/2\right)}{\left(\omega_{pi}-\omega_0\right)^2} &\approx \int_{-\infty}^{\infty} d\omega_{pi}\frac{\sin^2\left((\omega_{pi}-\omega_0)t/2\right)}{\left(\omega_{pi}-\omega_0\right)^2} \\ &= \frac{t}{2}\pi,\end{aligned} \tag{5.40}$$

leaving the probability of the electron with a going right continuum state as

$$\mathcal{P}_+ = \frac{4}{\hbar^2}\underbrace{\left|\bar{A}_{pi}\right|^2}_{\text{matrix element}}\underbrace{\left.\frac{dp}{d\omega_{pi}}\right|_{\bar{p}}}_{\text{density of states}}\frac{t}{2}\pi. \tag{5.41}$$

The $dp/d\omega_{pi}$ is something like "how many continuous states are associated with a transition from a discrete frequency interval."

We can also get this formally from eq. (5.39) with

$$\frac{\sin^2\left((\omega_{pi}-\omega_0)t/2\right)}{\left(\omega_{pi}-\omega_0\right)^2} \to \frac{t}{2}\pi\delta(\omega_{pi}-\omega_0), \tag{5.42}$$

so

$$\begin{aligned} c_p^{(1)}(t) &\to \frac{2\pi t}{\hbar^2}\left|\bar{A}_{pi}\right|^2 \delta(\omega_{pi} - \omega_0) \\ &= \frac{2\pi t}{\hbar}\left|\bar{A}_{pi}\right|^2 \delta(E_{pi} - \hbar\omega_0) \end{aligned} \tag{5.43}$$

where $\delta(ax) = \delta(x)/|a|$ has been used to pull in a factor of $\hbar$ into the delta.

The ratio of the coefficient to time is then

$$\frac{c_p^{(1)}(t)}{t} = \frac{2\pi}{\hbar}\left|\bar{A}_{pi}\right|^2 \delta(E_{pi} - \hbar\omega_0). \tag{5.44}$$

or "between friends"

$$\text{''}\frac{dc_p^{(1)}(t)}{dt}\text{''} = \frac{2\pi}{\hbar}\left|\bar{A}_{pi}\right|^2 \delta(E_{pi} - \hbar\omega_0), \tag{5.45}$$

roughly speaking we have a "rate" or transitions from the discrete into the continuous. Here "rate" is in quotes since it does not hold for small t.

This has been worked out for $\mathcal{P}_+$. This can also be done for $\mathcal{P}_-$, the probability that the electron will end up in a left trending continuum state.

While the above is not a formal derivation, but illustrates the form of what is called Fermi's golden rule. Namely that such a rate has the structure

$$\frac{2\pi}{\hbar} \times (\text{matrix element})^2 \times \text{energy conservation} \tag{5.46}$$

6

WKB METHOD

6.1 WKB (WENTZEL-KRAMERS-BRILLOUIN) METHOD

This is covered in §24 in the text [4]. Also §8 of [6].

We start with the 1D time independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2U}{dx^2} + V(x)U(x) = EU(x) \tag{6.1}$$

which we can write as

$$\frac{d^2U}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))U(x) = 0 \tag{6.2}$$

Consider a finite well potential as in fig. 6.1

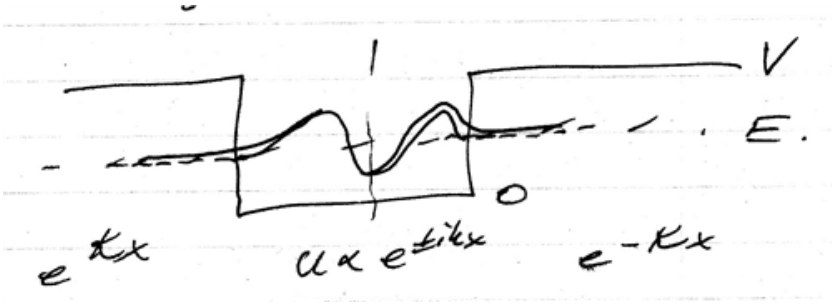

Figure 6.1: Finite well potential

With

$$\begin{aligned} k^2 &= \frac{2m(E-V)}{\hbar}, \qquad E > V \\ \kappa^2 &= \frac{2m(V-E)}{\hbar}, \qquad V > E, \end{aligned} \tag{6.3}$$

we have for a bound state within the well

$$U \propto e^{\pm ikx} \tag{6.4}$$

and for that state outside the well

$$U \propto e^{\pm \kappa x} \tag{6.5}$$

In general we can hope for something similar. Let us look for that something, but allow the constants k and κ to be functions of position

$$\begin{aligned} k^2(x) &= \frac{2m(E - V(x))}{\hbar}, \qquad E > V \\ \kappa^2(x) &= \frac{2m(V(x) - E)}{\hbar}, \qquad V > E. \end{aligned} \tag{6.6}$$

In terms of k Schrödinger's equation is just

$$\frac{d^2U(x)}{dx^2} + k^2(x)U(x) = 0. \tag{6.7}$$

We use the trial solution

$$U(x) = Ae^{i\phi(x)}, \tag{6.8}$$

allowing $\phi(x)$ to be complex

$$\phi(x) = \phi_R(x) + i\phi_I(x). \tag{6.9}$$

We need second derivatives

$$\begin{aligned} (e^{i\phi})'' &= (i\phi' e^{i\phi})' \\ &= (i\phi')^2 e^{i\phi} + i\phi'' e^{i\phi}, \end{aligned} \tag{6.10}$$

and plug back into our Schrödinger equation to obtain

$$-(\phi'(x))^2 + i\phi''(x) + k^2(x) = 0. \tag{6.11}$$

For the first round of approximation we assume

$$\phi''(x) \approx 0, \tag{6.12}$$

and obtain

$$(\phi'(x))^2 = k^2(x), \tag{6.13}$$

or

$$\phi'(x) = \pm k(x). \tag{6.14}$$

A second round of approximation we use eq. (6.14) and obtain

$$\phi''(x) = \pm k'(x) \tag{6.15}$$

Plugging back into eq. (6.11) we have

$$-(\phi'(x))^2 \pm ik'(x) + k^2(x) = 0, \tag{6.16}$$

Things get a little confusing here with the ± variation since we have to take a second set of square roots, so let's consider these separately.

Case I. positive root With $\phi' = +k$, we have

$$-(\phi'(x))^2 + ik'(x) + k^2(x) = 0, \tag{6.17}$$

or

$$\begin{aligned}\phi'(x) &= \pm\sqrt{+ik'(x) + k^2(x)} \\ &= \pm k(x)\sqrt{1 + i\frac{k'(x)}{k^2(x)}}.\end{aligned} \tag{6.18}$$

If k' is small compared to k^2

$$\frac{k'(x)}{k^2(x)} \ll 1, \tag{6.19}$$

then we have

$$\phi'(x) \approx \pm k(x)\left(1 + i\frac{k'(x)}{2k^2(x)}\right) = \pm\left(k(x) + i\frac{k'(x)}{2k(x)}\right) \tag{6.20}$$

Since we'd picked $\phi' \approx +k$ in this case, we pick the positive sign, and can now integrate

$$\begin{aligned}\phi(x) &= \int dx k(x) + i\int dx \frac{k'(x)}{2k(x)} + \ln \text{const} \\ &= \int dx k(x) + i\frac{1}{2}\ln k(x) + \ln \text{const}\end{aligned} \tag{6.21}$$

Going back to our wavefunction, for this $E > V(x)$ case we have

$$\begin{aligned}U(x) &\sim e^{i\phi(x)} \\ &= \exp\left(i\left(\int dx k(x) + i\frac{1}{2}\ln k(x) + \text{const}\right)\right) \\ &\sim \exp\left(i\left(\int dx k(x) + i\frac{1}{2}\ln k(x)\right)\right) \\ &= e^{i\int dx k(x)} e^{-\frac{1}{2}\ln k(x)}\end{aligned} \tag{6.22}$$

or

$$U(x) \propto \frac{1}{\sqrt{k(x)}} e^{i\int dx k(x)} \tag{6.23}$$

Case II: negative sign Now treat $\phi' \approx -k$. This gives us

$$\phi'(x) \approx \pm k(x)\left(1 - i\frac{k'(x)}{2k^2(x)}\right) = \pm\left(k(x) - i\frac{k'(x)}{2k(x)}\right) \tag{6.24}$$

This time we want the negative root to match $\phi' \approx -k$. Integrating, we have

$$\begin{aligned}i\phi(x) &= -i\int dx\left(k(x) - i\frac{k'(x)}{2k(x)}\right) \\ &= -i\int k(x)dx - \frac{1}{2}\int \frac{k'}{k}dx \\ &= -i\int k(x)dx - \frac{1}{2}\ln k + \ln \text{constant}\end{aligned} \tag{6.25}$$

This gives us

$$U(x) \propto \frac{1}{\sqrt{k(x)}} e^{-i\int dx k(x)} \tag{6.26}$$

Provided we have eq. (6.19), we can summarize these as

$$U(x) \propto \frac{1}{\sqrt{k(x)}} e^{\pm i \int dx k(x)} \tag{6.27}$$

It's not hard to show that for the $E < V(x)$ case we find

$$U(x) \propto \frac{1}{\sqrt{\kappa(x)}} e^{\pm \int dx \kappa(x)}, \tag{6.28}$$

this time, provided that our potential satisfies

$$\frac{\kappa'(x)}{\kappa^2(x)} \ll 1, \tag{6.29}$$

Validity

1. V(x) changes very slowly $\implies$ $k'(x)$ small, and $k(x) = \sqrt{2m(E - V(x))}/\hbar$.
2. E very far away from the potential $|(E - V(x))/V(x)| \gg 1$.

6.2 TURNING POINTS.

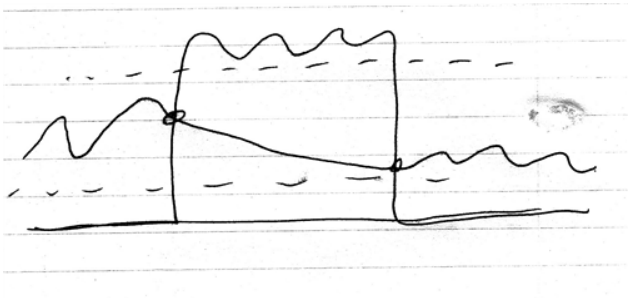

Figure 6.2: Example of a general potential

WKB will not work at the turning points in this figure since our main assumption was that

$$\left|\frac{k'(x)}{k^2(x)}\right| \ll 1 \tag{6.30}$$

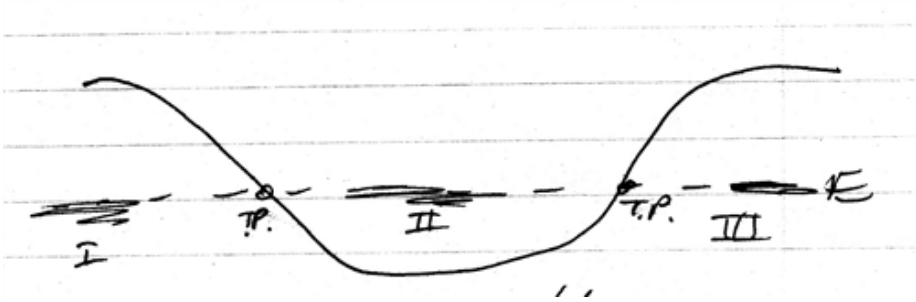

Figure 6.3: Turning points where WKB will not work

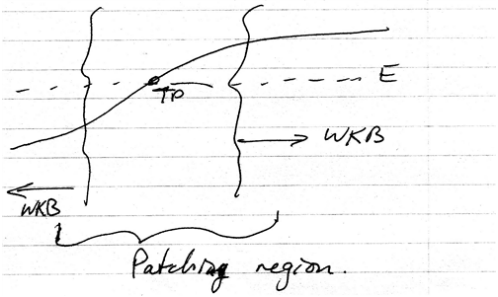

Figure 6.4: Diagram for patching method discussion

so we get into trouble where $k(x) \sim 0$. There are some methods for dealing with this. Our text as well as Griffiths give some examples, but they require Bessel functions and more complex mathematics.

The idea is that one finds the WKB solution in the regions of validity, and then looks for a polynomial solution in the patching region where we are closer to the turning point, probably requiring lookup of various special functions.

This power series method is also outlined in [19], where solutions to connect the regions are expressed in terms of Airy functions.

6.3 EXAMPLES

Example 6.1: Infinite well potential

Consider the potential

$$V(x) = \begin{cases} v(x) & \text{if } x \in [0, a] \\ \infty & \text{otherwise} \end{cases} \tag{6.31}$$

as illustrated in fig. 6.5

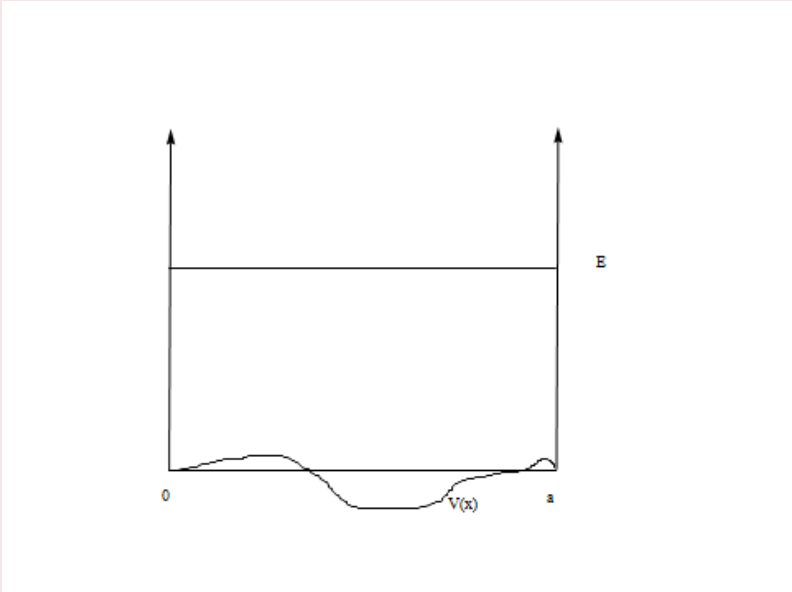

Figure 6.5: Arbitrary potential in an infinite well

Inside the well, we have

$$\psi(x) = \frac{1}{\sqrt{k(x)}} \left(C_+ e^{i \int_0^x k(x')dx'} + C_- e^{-i \int_0^x k(x')dx'} \right) \tag{6.32}$$

where

$$k(x) = \frac{1}{\hbar} \sqrt{2m(E - v(x))} \tag{6.33}$$

With

$$\phi(x) = e^{\int_0^x k(x')dx'} \tag{6.34}$$

We have

$$\begin{aligned}\psi(x) &= \frac{1}{\sqrt{k(x)}}\left(C_+(\cos\phi + i\sin\phi) + C_-(\cos\phi - i\sin\phi)\right)\\ &= \frac{1}{\sqrt{k(x)}}\left((C_+ + C_-)\cos\phi + i(C_+ - C_-)\sin\phi\right)\\ &= \frac{1}{\sqrt{k(x)}}\left((C_+ + C_-)\cos\phi + i(C_+ - C_-)\sin\phi\right)\\ &\equiv \frac{1}{\sqrt{k(x)}}\left(C_2\cos\phi + C_1\sin\phi\right),\end{aligned} \tag{6.35}$$

Where

$$\begin{aligned}C_2 &= C_+ + C_-\\ C_1 &= i(C_+ - C_-)\end{aligned} \tag{6.36}$$

Setting boundary conditions we have

$$\phi(0) = 0 \tag{6.37}$$

Noting that we have $\phi(0) = 0$, we have

$$\frac{1}{\sqrt{k(0)}}C_2 = 0 \tag{6.38}$$

So

$$\psi(x) \sim \frac{1}{\sqrt{k(x)}}\sin\phi \tag{6.39}$$

At the other boundary

$$\psi(a) = 0 \tag{6.40}$$

So we require

$$\sin\phi(a) = \sin(n\pi) \tag{6.41}$$

or

$$\frac{1}{\hbar}\int_0^a \sqrt{2m(E - v(x')}dx' = n\pi \tag{6.42}$$

This is called the Bohr-Sommerfeld condition.

Check with $v(x) = 0$.
We have

$$\frac{1}{\hbar}\sqrt{2mE}a = n\pi \tag{6.43}$$

or

$$E = \frac{1}{2m}\left(\frac{n\pi\hbar}{a}\right)^2 \tag{6.44}$$

Part II

SPIN, ANGULAR MOMENTUM, AND TWO PARTICLE SYSTEMS

7

COMPOSITE SYSTEMS

7.1 HILBERT SPACES

READING: §30 of the text [4] covers entangled states. The rest of the composite state background is buried somewhere in some of the advanced material sections. FIXME: what section?

Example, one spin one half particle and one spin one particle. We can describe either quantum mechanically, described by a pair of Hilbert spaces

$$H_1, \tag{7.1}$$

of dimension D_1

$$H_2, \tag{7.2}$$

of dimension D_2

Recall that a Hilbert space (finite or infinite dimensional) is the set of states that describe the system. There were some additional details (completeness, normalizable, $L2$ integrable, ...) not really covered in the physics curriculum, but available in mathematical descriptions.

We form the composite (Hilbert) space

$$H = H_1 \otimes H_2 \tag{7.3}$$

$$H_1 : \left|\phi_1^{(i)}\right\rangle \tag{7.4}$$

for any ket in H_1

$$|I\rangle = \sum_{i=1}^{D_1} c_i \left|\phi_1^{(i)}\right\rangle \tag{7.5}$$

where

$$\left\langle\phi_1^{(i)}\middle|\phi_1^{(j)}\right\rangle = \delta^{ij} \tag{7.6}$$

Similarly

$$H_2 : \left|\phi_2^{(i)}\right\rangle \tag{7.7}$$

for any ket in H_2

$$|II\rangle = \sum_{i=1}^{D_2} d_i \left|\phi_2^{(i)}\right\rangle \tag{7.8}$$

where

$$\left\langle\phi_2^{(i)}\middle|\phi_2^{(j)}\right\rangle = \delta^{ij} \tag{7.9}$$

The composite Hilbert space has dimension $D_1 D_2$ basis kets:

$$\left|\phi_1^{(i)}\right\rangle \otimes \left|\phi_2^{(j)}\right\rangle = \left|\phi^{(ij)}\right\rangle, \tag{7.10}$$

where

$$\left\langle\phi^{(ij)}\middle|\phi^{(kl)}\right\rangle = \delta^{ik}\delta^{jl}. \tag{7.11}$$

Any ket in H can be written

$$\begin{aligned} |\psi\rangle &= \sum_{i=1}^{D_1}\sum_{j=1}^{D_2} f_{ij} \left|\phi_1^{(i)}\right\rangle \otimes \left|\phi_2^{(j)}\right\rangle \\ &= \sum_{i=1}^{D_1}\sum_{j=1}^{D_2} f_{ij} \left|\phi^{(ij)}\right\rangle. \end{aligned} \tag{7.12}$$

Direct product of kets:

$$\begin{aligned} |I\rangle \otimes |II\rangle &\equiv \sum_{i=1}^{D_1}\sum_{j=1}^{D_2} c_i d_j \left|\phi_1^{(i)}\right\rangle \otimes \left|\phi_2^{(j)}\right\rangle \\ &= \sum_{i=1}^{D_1}\sum_{j=1}^{D_2} c_i d_j \left|\phi^{(ij)}\right\rangle \end{aligned} \tag{7.13}$$

If $|\psi\rangle$ in H cannot be written as $|I\rangle \otimes |II\rangle$, then $|\psi\rangle$ is said to be "entangled". FIXME: insert a concrete example of this, with some low dimension.

7.2 OPERATORS

With operators O_1 and O_2 on the respective Hilbert spaces. We would now like to build

$$O_1 \otimes O_2 \tag{7.14}$$

If one defines

$$O_1 \otimes O_2 \equiv \sum_{i=1}^{D_1} \sum_{j=1}^{D_2} f_{ij} \left| O_1 \phi_1^{(i)} \right\rangle \otimes \left| O_2 \phi_2^{(j)} \right\rangle \tag{7.15}$$

Q:Can every operator that can be defined on the composite space have a representation of this form? No.

Special cases. The identity operators. Suppose that

$$|\psi\rangle = \sum_{i=1}^{D_1} \sum_{j=1}^{D_2} f_{ij} \left| \phi_1^{(i)} \right\rangle \otimes \left| \phi_2^{(j)} \right\rangle \tag{7.16}$$

then

$$(O_1 \otimes \mathcal{I}_2) |\psi\rangle = \sum_{i=1}^{D_1} \sum_{j=1}^{D_2} f_{ij} \left| O_1 \phi_1^{(i)} \right\rangle \otimes \left| \phi_2^{(j)} \right\rangle \tag{7.17}$$

Example 7.1: A commutator

Can do other operations. Example:

$$[O_1 \otimes \mathcal{I}_2, \mathcal{I}_1 \otimes O_2] = 0 \tag{7.18}$$

Let us verify this one. Suppose that our state has the representation

$$|\psi\rangle = \sum_{i=1}^{D_1} \sum_{j=1}^{D_2} f_{ij} \left| \phi_1^{(i)} \right\rangle \otimes \left| \phi_2^{(j)} \right\rangle \tag{7.19}$$

so that the action on this ket from the composite operations are

$$\begin{aligned}(O_1 \otimes \mathcal{I}_2)\,|\psi\rangle &= \sum_{i=1}^{D_1}\sum_{j=1}^{D_2} f_{ij}\left|O_1\phi_1^{(i)}\right\rangle \otimes \left|\phi_2^{(j)}\right\rangle \\ (\mathcal{I}_1 \otimes O_2)\,|\psi\rangle &= \sum_{i=1}^{D_1}\sum_{j=1}^{D_2} f_{ij}\left|\phi_1^{(i)}\right\rangle \otimes \left|O_2\phi_2^{(j)}\right\rangle\end{aligned} \tag{7.20}$$

Our commutator is

$$\begin{aligned}&\left[(O_1 \otimes \mathcal{I}_2), (\mathcal{I}_1 \otimes O_2)\right]|\psi\rangle \\ &= (O_1 \otimes \mathcal{I}_2)(\mathcal{I}_1 \otimes O_2)\,|\psi\rangle - (\mathcal{I}_1 \otimes O_2)(O_1 \otimes \mathcal{I}_2)\,|\psi\rangle \\ &= (O_1 \otimes \mathcal{I}_2)\sum_{i=1}^{D_1}\sum_{j=1}^{D_2} f_{ij}\left|\phi_1^{(i)}\right\rangle \otimes \left|O_2\phi_2^{(j)}\right\rangle - (\mathcal{I}_1 \otimes O_2)\sum_{i=1}^{D_1}\sum_{j=1}^{D_2} f_{ij}\left|O_1\phi_1^{(i)}\right\rangle \otimes \left|\phi_2^{(j)}\right\rangle \\ &= \sum_{i=1}^{D_1}\sum_{j=1}^{D_2} f_{ij}\left|O_1\phi_1^{(i)}\right\rangle \otimes \left|O_2\phi_2^{(j)}\right\rangle - \sum_{i=1}^{D_1}\sum_{j=1}^{D_2} f_{ij}\left|O_1\phi_1^{(i)}\right\rangle \otimes \left|O_2\phi_2^{(j)}\right\rangle \\ &= 0. \qquad \square\end{aligned} \tag{7.21}$$

7.3 GENERALIZATIONS

Can generalize to

$$H_1 \otimes H_2 \otimes H_3 \otimes \cdots \tag{7.22}$$

Can also start with H and seek factor spaces. If H is not prime there are, in general, many ways to find factor spaces

$$H = H_1 \otimes H_2 = H_1' \otimes H_2' \tag{7.23}$$

A ket $|\psi\rangle$, if unentangled in the first factor space, then it will be in general entangled in a second space. Thus ket entanglement is not a property of the ket itself, but instead is intrinsically related to the space in which it is represented.

7.4 RECALLING THE STERN-GERLACH SYSTEM FROM PHY354

We had one example of a composite system in phy356 that I recall. It was related to states of the silver atoms in a Stern Gerlach apparatus, where we had one state from the Hamiltonian that

governs position and momentum and another from the Hamiltonian for the spin, where each of these states was considered separately.

This makes me wonder what would the Hamiltonian for a system (say a single electron) that includes both spin and position/momentum would look like, and how is it that one can solve this taking spin and non-spin states separately?

Professor Sipe, when asked said of this

"It is complicated because not only would the spin of the electron interact with the magnetic field, but its translational motion would respond to the magnetic field too. A simpler case is a neutral atom with an electron with an unpaired spin. Then there is no Lorentz force on the atom itself. The Hamiltonian is just the sum of a free particle Hamiltonian and a Zeeman term due to the spin interacting with the magnetic field. This is precisely the Stern-Gerlach problem"

I did not remember what the Zeeman term looked like, but wikipedia does [20], and it is the magnetic field interaction

$$-\boldsymbol{\mu} \cdot \mathbf{B} \tag{7.24}$$

that we get when we gauge transform the Dirac equation for the electron as covered in §36.4 of the text (also introduced in chapter 6, which was not covered in class). That does not look too much like how we studied the Stern-Gerlach problem? I thought that for that problem we had a Hamiltonian of the form

$$H = a_{ij} |i\rangle \langle j| \tag{7.25}$$

It is not clear to me how this ket-bra Hamiltonian and the Zeeman Hamiltonian are related (ie: the spin Hamiltonians that we used in 356 and were on old 356 exams were all pulled out of magic hats and it was not obvious where these came from).

FIXME: incorporate what I got out of the email thread with the TA and prof on this question.

8

SPIN AND SPINORS

8.1 GENERATORS

Covered in §26 of the text [4].

Example 8.1: Time translation

$$|\psi(t)\rangle = e^{-iHt/\hbar}\,|\psi(0)\rangle\,. \tag{8.1}$$

The Hamiltonian "generates" evolution (or translation) in time.

Example 8.2: Spatial translation

$$|\mathbf{r}+\mathbf{a}\rangle = e^{-i\mathbf{a}\cdot\mathbf{P}/\hbar}\,|\mathbf{r}\rangle\,. \tag{8.2}$$

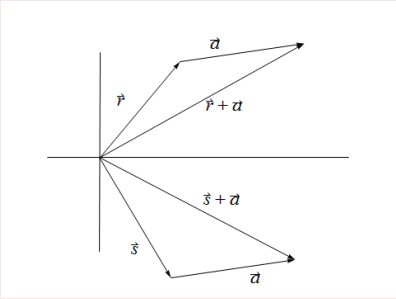

Figure 8.1: Vector translation

P is the operator that generates translations. Written out, we have

$$\begin{aligned} e^{-i\mathbf{a}\cdot\mathbf{P}/\hbar} &= e^{-i(a_xP_x+a_yP_y+a_zP_z)/\hbar} \\ &= e^{-ia_xP_x/\hbar}e^{-ia_yP_y/\hbar}e^{-ia_zP_z/\hbar}, \end{aligned} \tag{8.3}$$

where the factorization was possible because P_x, P_y, and P_z commute

$$[P_i, P_j] = 0, \tag{8.4}$$

for any i, j (including $i = i$ as I dumbly questioned in class ... this is a commutator, so $[P_i, P_j] = P_i P_i - P_i P_i = 0$).

The fact that the P_i commute means that successive translations can be done in any order and have the same result.

In class we were rewarded with a graphic demo of translation component commutation as Professor Sipe pulled a giant wood carving of a cat (or tiger?) out from beside the desk and proceeded to translate it around on the desk in two different orders, with the cat ending up in the same place each time.

Exponential commutation Note that in general

$$e^{A+B} \neq e^A e^B, \tag{8.5}$$

unless $[A, B] = 0$. To show this one can compare

$$\begin{aligned} e^{A+B} &= 1 + A + B + \frac{1}{2}(A + B)^2 + \cdots \\ &= 1 + A + B + \frac{1}{2}(A^2 + AB + BA + B^2) + \cdots \end{aligned} \tag{8.6}$$

and

$$\begin{aligned} e^A e^B &= \left(1 + A + \frac{1}{2}A^2 + \cdots\right)\left(1 + B + \frac{1}{2}B^2 + \cdots\right) \\ &= 1 + A + B + \frac{1}{2}(A^2 + 2AB + B^2) + \cdots \end{aligned} \tag{8.7}$$

Comparing the second order (for example) we see that we must have for equality

$$AB + BA = 2AB, \tag{8.8}$$

or

$$BA = AB, \tag{8.9}$$

or

$$[A, B] = 0 \tag{8.10}$$

Translating a ket If we consider the quantity

$$e^{-i\mathbf{a}\cdot\mathbf{P}/\hbar}\,|\psi\rangle = \left|\psi'\right\rangle, \tag{8.11}$$

does this ket "translated" by $\mathbf{a}$ make any sense? The vector $\mathbf{a}$ lives in a 3D space and our ket $|\psi\rangle$ lives in Hilbert space. A quantity like this deserves some careful thought and is the subject of some such thought in the Interpretations of Quantum mechanics course. For now, we can think of the operator and ket as a "gadget" that prepares a state.

A student in class pointed out that $|\psi\rangle$ can be dependent on many degrees of freedom, for example, the positions of eight different particles. This translation gadget in such a case acts on the whole kit and caboodle.

Now consider the matrix element

$$\left\langle \mathbf{r}\middle|\psi'\right\rangle = \langle \mathbf{r}|\, e^{-i\mathbf{a}\cdot\mathbf{P}/\hbar}\,|\psi\rangle\,. \tag{8.12}$$

Note that

$$\begin{aligned}\langle \mathbf{r}|\, e^{-i\mathbf{a}\cdot\mathbf{P}/\hbar} &= \left(e^{i\mathbf{a}\cdot\mathbf{P}/\hbar}\,|\mathbf{r}\rangle\right)^\dagger \\ &= \left(|\mathbf{r}-\mathbf{a}\rangle\right)^\dagger,\end{aligned} \tag{8.13}$$

so

$$\left\langle \mathbf{r}\middle|\psi'\right\rangle = \langle \mathbf{r}-\mathbf{a}|\psi\rangle\,, \tag{8.14}$$

or

$$\psi'(\mathbf{r}) = \psi(\mathbf{r} - \mathbf{a}) \tag{8.15}$$

This is what we expect of a translated function, as illustrated in fig. 8.2

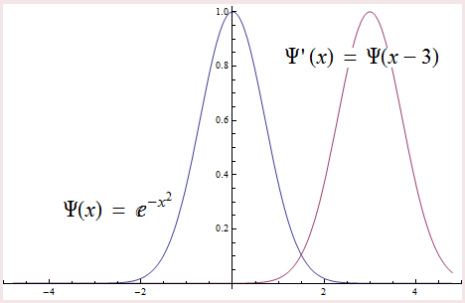

Figure 8.2: Active spatial translation

Example 8.3: Spatial rotation

We have been introduced to the angular momentum operator

$$\mathbf{L} = \mathbf{R} \times \mathbf{P}, \tag{8.16}$$

where

$$\begin{aligned} L_x &= YP_z - ZP_y \\ L_y &= ZP_x - XP_z \\ L_z &= XP_y - YP_x. \end{aligned} \tag{8.17}$$

We also found that

$$[L_i, L_j] = i\hbar \sum_k \epsilon_{ijk} L_k. \tag{8.18}$$

These non-zero commutators show that the components of angular momentum do not commute.

Define

$$|\mathcal{R}(\mathbf{r})\rangle = e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{L}/\hbar}\,|\mathbf{r}\rangle\,. \tag{8.19}$$

This is the vector that we get by actively rotating the vector $\mathbf{r}$ by an angle θ counter-clockwise about $\hat{\mathbf{n}}$, as in fig. 8.3

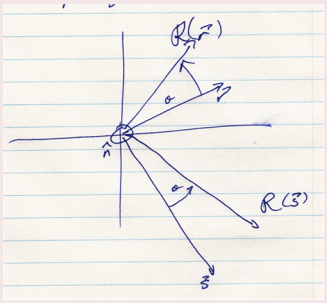

Figure 8.3: Active vector rotations

An active rotation rotates the vector, leaving the coordinate system fixed, whereas a passive rotation is one for which the coordinate system is rotated, and the vector is left fixed.

Note that rotations do not commute. Suppose that we have a pair of rotations as in fig. 8.4

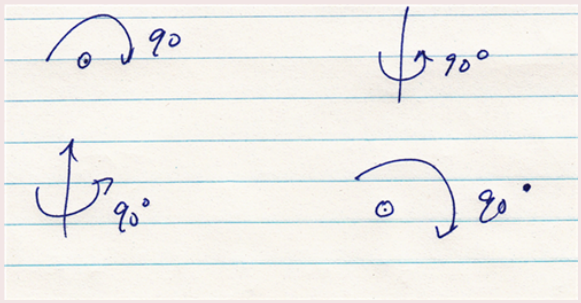

Figure 8.4: A example pair of non-commuting rotations

Again, we get the graphic demo, with Professor Sipe rotating the big wooden cat sculpture. Did he bring that in to class just to make this point (too bad I missed the first couple minutes of the lecture).

Rather amusingly, he points out that most things in life do not commute. We get much different results if we apply the operations of putting water into the teapot and turning on the stove in different orders.

Rotating a ket With a rotation gadget

$$\left|\psi'\right\rangle = e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{L}/\hbar}\left|\psi\right\rangle, \tag{8.20}$$

we can form the matrix element

$$\left\langle\mathbf{r}\middle|\psi'\right\rangle = \left\langle\mathbf{r}\right| e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{L}/\hbar}\left|\psi\right\rangle. \tag{8.21}$$

In this we have

$$\begin{aligned}\left\langle\mathbf{r}\right| e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{L}/\hbar} &= \left(e^{i\theta\hat{\mathbf{n}}\cdot\mathbf{L}/\hbar}\left|\mathbf{r}\right\rangle\right)^\dagger \\ &= \left(\left|\mathcal{R}^{-1}(\mathbf{r})\right\rangle\right)^\dagger,\end{aligned} \tag{8.22}$$

so

$$\left\langle\mathbf{r}\middle|\psi'\right\rangle = \left\langle\mathcal{R}^{-1}(\mathbf{r})\middle|\psi'\right\rangle, \tag{8.23}$$

or

$$\psi'(\mathbf{r}) = \psi(\mathcal{R}^{-1}(\mathbf{r})) \tag{8.24}$$

8.2 GENERALIZATIONS

Recall what you did last year, where H, $\mathbf{P}$, and $\mathbf{L}$ were defined mechanically. We found

- H generates time evolution (or translation in time).
- $\mathbf{P}$ generates spatial translation.
- $\mathbf{L}$ generates spatial rotation.

For our mechanical definitions we have

$$[P_i, P_j] = 0, \tag{8.25}$$

and

$$[L_i, L_j] = i\hbar\sum_k \epsilon_{ijk}L_k. \tag{8.26}$$

These are the relations that show us the way translations and rotations combine. We want to move up to a higher plane, a new level of abstraction. To do so we define H as the operator that generates time evolution. If we have a theory that covers the behavior of how anything evolves in time, H encodes the rules for this time evolution.

Define $\mathbf{P}$ as the operator that generates translations in space.

Define $\mathbf{J}$ as the operator that generates rotations in space.

In order that these match expectations, we require

$$[P_i, P_j] = 0, \tag{8.27}$$

and

$$[J_i, J_j] = i\hbar \sum_k \epsilon_{ijk} J_k. \tag{8.28}$$

In the simple theory of a spin less particle we have

$$\mathbf{J} \equiv \mathbf{L} = \mathbf{R} \times \mathbf{P}. \tag{8.29}$$

We actually need a generalization of this since this is, in fact, not good enough, even for low energy physics.

Many component wave functions We are free to construct tuples of spatial vector functions like

$$\begin{bmatrix} \Psi_I(\mathbf{r}, t) \\ \Psi_{II}(\mathbf{r}, t) \end{bmatrix}, \tag{8.30}$$

or

$$\begin{bmatrix} \Psi_I(\mathbf{r}, t) \\ \Psi_{II}(\mathbf{r}, t) \\ \Psi_{III}(\mathbf{r}, t) \end{bmatrix}, \tag{8.31}$$

etc.

We will see that these behave qualitatively different than one component wave functions. We also do not have to be considering multiple particle wave functions, but just one particle that requires three functions in $\mathbb{R}^3$ to describe it (ie: we are moving in on spin).

Question: Do these live in the same vector space?

Answer: We will get to this.

A classical analogy "There is only bad analogies, since if the are good they would be describing the same thing. We can however, produce some useful bad analogies"

1. A temperature field

$$T(\mathbf{r}) \tag{8.32}$$

2. Electric field

$$\begin{bmatrix} E_x(\mathbf{r}) \\ E_y(\mathbf{r}) \\ E_z(\mathbf{r}) \end{bmatrix} \tag{8.33}$$

These behave in a much different way. If we rotate a scalar field like $T(\mathbf{r})$ as in fig. 8.5

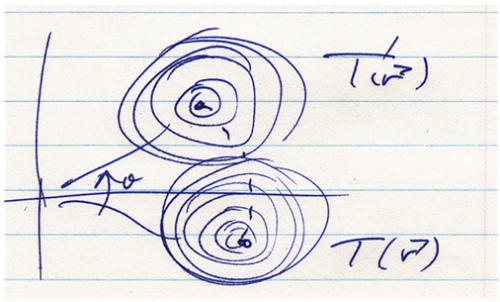

Figure 8.5: Rotated temperature (scalar) field

Suppose we have a temperature field generated by, say, a match. Rotating the match above, we have

$$T'(\mathbf{r}) = T(\mathcal{R}^{-1}(\mathbf{r})). \tag{8.34}$$

Compare this to the rotation of an electric field, perhaps one produced by a capacitor, as in fig. 8.6

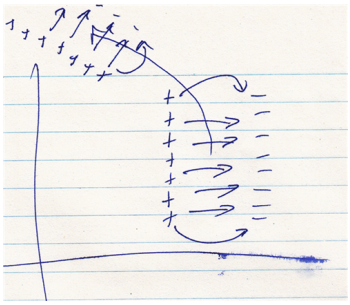

Figure 8.6: Rotating a capacitance electric field

Is it true that we have

$$\begin{bmatrix} E_x(\mathbf{r}) \\ E_y(\mathbf{r}) \\ E_z(\mathbf{r}) \end{bmatrix} \stackrel{?}{=} \begin{bmatrix} E_x(\mathcal{R}^{-1}(\mathbf{r})) \\ E_y(\mathcal{R}^{-1}(\mathbf{r})) \\ E_z(\mathcal{R}^{-1}(\mathbf{r})) \end{bmatrix} \tag{8.35}$$

No. Because the components get mixed as well as the positions at which those components are evaluated.

We will work with many component wave functions, some of which will behave like vectors, and will have to develop the methods and language to tackle this.

8.3 MULTIPLE WAVEFUNCTION SPACES

Reading: See §26.5 in the text [4].

We identified

$$\psi(\mathbf{r}) = \langle \mathbf{r}|\psi\rangle \tag{8.36}$$

with improper basis kets

$$|\mathbf{r}\rangle \tag{8.37}$$

Now introduce many function spaces

$$\begin{bmatrix} \psi_1(\mathbf{r}) \\ \psi_2(\mathbf{r}) \\ \vdots \\ \psi_\gamma(\mathbf{r}) \end{bmatrix} \tag{8.38}$$

with improper (unnormalizable) basis kets

$$|\mathbf{r}\alpha\rangle\,, \qquad \alpha \in 1, 2, ...\gamma \tag{8.39}$$

$$\psi_\alpha(\mathbf{r}) = \langle \mathbf{r}\alpha|\psi\rangle \tag{8.40}$$

for an abstract ket $|\psi\rangle$
We will try taking this Hilbert space

$$H = H_o \otimes H_s \tag{8.41}$$

Where H_o is the Hilbert space of "scalar" QM, “o” orbital and translational motion, associated with kets $|\mathbf{r}\rangle$ and H_s is the Hilbert space associated with the γ components $|\alpha\rangle$. This latter space we will label the “spin” or “internal physics” (class suggestion: or perhaps intrinsic). This is “unconnected” with translational motion.

We build up the basis kets for H by direct products

$$|\mathbf{r}\alpha\rangle = |\mathbf{r}\rangle \otimes |\alpha\rangle \tag{8.42}$$

Now, for a rotated ket we seek a general angular momentum operator $\mathbf{J}$ such that

$$\left|\psi'\right\rangle = e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}\,|\psi\rangle \tag{8.43}$$

where

$$\mathbf{J} = \mathbf{L} + \mathbf{S}, \tag{8.44}$$

where $\mathbf{L}$ acts over kets in H_o, “orbital angular momentum”, and $\mathbf{S}$ is the “spin angular momentum”, acting on kets in H_s.

Strictly speaking this would be written as direct products involving the respective identities

$$\mathbf{J} = \mathbf{L} \otimes I_s + I_o \otimes \mathbf{S}. \tag{8.45}$$

We require

$$[J_i, J_j] = i\hbar \sum \epsilon_{ijk} J_k \tag{8.46}$$

Since **L** and **S** "act over separate Hilbert spaces". Since these come from legacy operators

$$[L_i, S_j] = 0 \tag{8.47}$$

We also know that

$$[L_i, L_j] = i\hbar \sum \epsilon_{ijk} L_k \tag{8.48}$$

so

$$[S_i, S_j] = i\hbar \sum \epsilon_{ijk} S_k, \tag{8.49}$$

as expected. We could, in principle, have more complicated operators, where this would not be true. This is a proposal of sorts. Given such a definition of operators, let us see where we can go with it.

For matrix elements of **L** we have

$$\langle \mathbf{r}| L_x \left|\mathbf{r}'\right\rangle = -i\hbar \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right) \delta(\mathbf{r} - \mathbf{r}') \tag{8.50}$$

What are the matrix elements of $\langle \alpha| S_i |\alpha'\rangle$? From the commutation relationships we know

$$\sum_{\alpha''=1}^{\gamma} \langle \alpha| S_i \left|\alpha''\right\rangle \left\langle \alpha''\right| S_j \left|\alpha'\right\rangle - \sum_{\alpha''=1}^{\gamma} \langle \alpha| S_j \left|\alpha''\right\rangle \left\langle \alpha''\right| S_i \left|\alpha'\right\rangle = i\hbar \sum_k \epsilon_{ijk} \langle \alpha| S_k \left|\alpha''\right\rangle \tag{8.51}$$

We see that our matrix element is tightly constrained by our choice of commutator relationships. We have γ^2 such matrix elements, and it turns out that it is possible to choose (or find) matrix elements that satisfy these constraints?

The $\langle \alpha| S_i |\alpha'\rangle$ matrix elements that satisfy these constraints are found by imposing the commutation relations

$$[S_i, S_j] = i\hbar \sum \epsilon_{ijk} S_k, \tag{8.52}$$

and with

$$S^2 = \sum_j S_j^2, \tag{8.53}$$

(this is just a definition). We find

$$\left[S^2, S_i\right] = 0 \tag{8.54}$$

and seeking eigenkets

$$\begin{aligned} S^2 \left|sm_s\right\rangle &= s(s+1)\hbar^2 \left|sm_s\right\rangle \\ S_z \left|sm_s\right\rangle &= \hbar m_s \left|sm_s\right\rangle \end{aligned} \tag{8.55}$$

Find solutions for $s = 1/2, 1, 3/2, 2, \cdots$, where $m_s \in \{-s, \cdots, s\}$. ie. $2s+1$ possible vectors $\left|sm_s\right\rangle$ for a given s.

$$\begin{aligned} s = \frac{1}{2} &\implies \gamma = 2 \\ s = 1 &\implies \gamma = 3 \\ s = \frac{3}{2} &\implies \gamma = 4 \end{aligned} \tag{8.56}$$

We start with the algebra (mathematically the Lie algebra), and one can compute the Hilbert spaces that are consistent with these algebraic constraints.

We assume that for any type of given particle S is fixed, where this has to do with the nature of the particle.

$$\begin{aligned} s = \frac{1}{2} &\quad \text{A spin } 1/2 \text{ particle} \\ s = 1 &\quad \text{A spin 1 particle} \\ s = \frac{3}{2} &\quad \text{A spin } 3/2 \text{ particle} \end{aligned} \tag{8.57}$$

S is fixed once we decide that we are talking about a specific type of particle.

A non-relativistic particle in this framework has two nondynamical quantities. One is the mass m and we now introduce a new invariant, the spin s of the particle.

This has been introduced as a kind of strategy. It is something that we are going to try, and it turns out that it does. This agrees well with experiment.

In 1939 Wigner asked, "what constraints do I get if I constrain the constraints of quantum mechanics with special relativity." It turns out that in the non-relativistic limit, we get just this.

There is a subtlety here, because we get into some logical trouble with the photon with a rest mass of zero ($m = 0$ is certainly allowed as a value of our invariant m above). We can not stop or slow down a photon, so orbital angular momentum is only a conceptual idea. Really, the orbital angular momentum and the spin angular momentum cannot be separated out for a photon, so talking of a spin 1 particle really means spin as in $\mathbf{J}$, and not spin as in $\mathbf{L}$.

Spin one half particles Reading: See §26.6 in the text [4].

Let us start talking about the simplest case. This includes electrons, all leptons (integer spin particles like photons and the weakly interacting W and Z bosons), and quarks.

$$\begin{aligned} s &= \frac{1}{2} \\ m_s &= \pm\frac{1}{2} \end{aligned} \tag{8.58}$$

states

$$|sm_s\rangle = \left|\frac{1}{2}, \frac{1}{2}\right\rangle, \left|\frac{1}{2}, -\frac{1}{2}\right\rangle \tag{8.59}$$

Note there is a convention

$$\begin{aligned} \left|\frac{1}{2}\frac{\overline{1}}{2}\right\rangle &= \left|\frac{1}{2}, -\frac{1}{2}\right\rangle \\ \left|\frac{1}{2}\frac{1}{2}\right\rangle &= \left|\frac{1}{2}\frac{1}{2}\right\rangle \end{aligned} \tag{8.60}$$

$$\begin{aligned} S^2\left|\frac{1}{2}m_s\right\rangle &= \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\left|\frac{1}{2}m_s\right\rangle \\ &= \frac{3}{4}\hbar^2\left|\frac{1}{2}m_s\right\rangle \end{aligned} \tag{8.61}$$

$$S_z\left|\frac{1}{2}m_s\right\rangle = m_s\hbar\left|\frac{1}{2}m_s\right\rangle \tag{8.62}$$

For shorthand

$$\begin{aligned} \left|\frac{1}{2}\frac{1}{2}\right\rangle &= |+\rangle \\ \left|\frac{1}{2}\frac{\overline{1}}{2}\right\rangle &= |-\rangle \end{aligned} \tag{8.63}$$

$$S^2 \to \frac{3}{4}\hbar^2\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{8.64}$$

$$S_z \to \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{8.65}$$

One can easily work out from the commutation relationships that

$$S_x \to \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \tag{8.66}$$

$$S_y \to \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \tag{8.67}$$

We will start with adding **L** into the mix on Wednesday.

9

REPRESENTATION OF TWO STATE KETS AND PAULI SPIN MATRICES

9.1 REPRESENTATION OF KETS

Reading: §5.1 - §5.9 and §26 in [4].

We found the representations of the spin operators

$$S_x \to \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \tag{9.1}$$

$$S_y \to \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \tag{9.2}$$

$$S_z \to \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{9.3}$$

How about kets? For example for $|\chi\rangle \in H_s$

$$|\chi\rangle \to \begin{bmatrix} \langle +|\chi\rangle \\ \langle -|\chi\rangle \end{bmatrix}, \tag{9.4}$$

and

$$|+\rangle \to \begin{bmatrix} 1 \\ 0 \end{bmatrix} \tag{9.5}$$

$$|0\rangle \to \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{9.6}$$

So, for example

$$S_y|+\rangle \to \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{i\hbar}{2}\begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{9.7}$$

Kets in $H_o \otimes H_s$

$$|\psi\rangle \to \begin{bmatrix} \langle \mathbf{r}+|\psi\rangle \\ \langle \mathbf{r}-|\psi\rangle \end{bmatrix} = \begin{bmatrix} \psi_+(\mathbf{r}) \\ \psi_-(\mathbf{r}) \end{bmatrix}. \tag{9.8}$$

This is a "spinor"
Put

$$\begin{aligned} \langle \mathbf{r}\pm|\psi\rangle &= \psi_\pm(\mathbf{r}) \\ &= \psi_+ \begin{bmatrix} 1 \\ 0 \end{bmatrix} + \psi_- \begin{bmatrix} 0 \\ 1 \end{bmatrix} \end{aligned} \tag{9.9}$$

with

$$\langle \psi|\psi\rangle = 1 \tag{9.10}$$

Use

$$\begin{aligned} I &= I_o \otimes I_s \\ &= \int d^3\mathbf{r}\, |\mathbf{r}\rangle\langle\mathbf{r}| \otimes \left(|+\rangle\langle+| + |-\rangle\langle-|\right) \\ &= \int d^3\mathbf{r}\, |\mathbf{r}\rangle\langle\mathbf{r}| \otimes \sum_{\sigma=\pm} |\sigma\rangle\langle\sigma| \\ &= \sum_{\sigma=\pm} \int d^3\mathbf{r}\, |\mathbf{r}\sigma\rangle\langle\mathbf{r}\sigma| \end{aligned} \tag{9.11}$$

So

$$\begin{aligned} \langle\psi|\, I\, |\psi\rangle &= \sum_{\sigma=\pm} \int d^3\mathbf{r}\, \langle\psi|\mathbf{r}\sigma\rangle\langle\mathbf{r}\sigma|\psi\rangle \\ &= \int d^3\mathbf{r}\left(|\psi_+(\mathbf{r})|^2 + |\psi_-(\mathbf{r})|^2\right) \end{aligned} \tag{9.12}$$

Alternatively

$$\begin{aligned}|\psi\rangle &= I\,|\psi\rangle \\ &= \int d^3\mathbf{r} \sum_{\sigma=\pm} |\mathbf{r}\sigma\rangle\,\langle\mathbf{r}\sigma|\psi\rangle \\ &= \sum_{\sigma=\pm}\left(\int d^3\mathbf{r}\psi_\sigma(\mathbf{r})\right)|\mathbf{r}\sigma\rangle \\ &= \sum_{\sigma=\pm}\left(\int d^3\mathbf{r}\psi_\sigma(\mathbf{r})\,|\mathbf{r}\rangle\right)\otimes|\sigma\rangle\end{aligned} \tag{9.13}$$

In braces we have a ket in H_o, let us call it

$$|\psi_\sigma\rangle = \int d^3\mathbf{r}\psi_\sigma(\mathbf{r})\,|\mathbf{r}\rangle\,, \tag{9.14}$$

then

$$|\psi\rangle = |\psi_+\rangle\,|+\rangle + |\psi_-\rangle\,|-\rangle \tag{9.15}$$

where the direct product $\otimes$ is implied.
We can form a ket in H_s as

$$\langle\mathbf{r}|\psi\rangle = \psi_+(\mathbf{r})\,|+\rangle + \psi_-(\mathbf{r})\,|-\rangle \tag{9.16}$$

An operator O_o which acts on H_o alone can be promoted to $O_o \otimes I_s$, which is now an operator that acts on $H_o \otimes H_s$. We are sometimes a little cavalier in notation and leave this off, but we should remember this.

$$O_o\,|\psi\rangle = (O_o\,|\psi+\rangle)\,|+\rangle + (O_o\,|\psi+\rangle)\,|+\rangle \tag{9.17}$$

and likewise

$$O_s\,|\psi\rangle = |\psi+\rangle\,(O_s\,|+\rangle) + |\psi-\rangle\,(O_s\,|-\rangle) \tag{9.18}$$

and

$$O_oO_s\,|\psi\rangle = (O_o\,|\psi+\rangle)(O_s\,|+\rangle) + (O_o\,|\psi-\rangle)(O_s\,|-\rangle) \tag{9.19}$$

Suppose we want to rotate a ket, we do this with a full angular momentum operator

$$e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}|\psi\rangle = e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{L}/\hbar}e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{S}/\hbar}|\psi\rangle \tag{9.20}$$

(recalling that $\mathbf{L}$ and $\mathbf{S}$ commute)
So

$$e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}|\psi\rangle = (e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{L}/\hbar}|\psi+\rangle)(e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{S}/\hbar}|+\rangle) + (e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{L}/\hbar}|\psi-\rangle)(e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{S}/\hbar}|-\rangle) \tag{9.21}$$

A simple example

$$|\psi\rangle = |\psi_+\rangle|+\rangle + |\psi_-\rangle|-\rangle \tag{9.22}$$

Suppose

$$|\psi_+\rangle = \alpha|\psi_0\rangle \tag{9.23}$$
$$|\psi_-\rangle = \beta|\psi_0\rangle \tag{9.24}$$

where

$$|\alpha|^2 + |\beta|^2 = 1 \tag{9.25}$$

Then

$$|\psi\rangle = |\psi_0\rangle|\chi\rangle \tag{9.26}$$

where

$$|\chi\rangle = \alpha|+\rangle + \beta|-\rangle \tag{9.27}$$

for

$$\langle\psi|\psi\rangle = 1, \tag{9.28}$$

$$\langle\psi_0|\psi_0\rangle\langle\chi|\chi\rangle = 1 \tag{9.29}$$

so

$$\langle\psi_0|\psi_0\rangle = 1 \tag{9.30}$$

We are going to concentrate on the unentangled state of eq. (9.26).

- How about with

$$|\alpha|^2 = 1, \beta = 0 \tag{9.31}$$

$|\chi\rangle$ is an eigenket of S_z with eigenvalue $\hbar/2$.

-

$$|\beta|^2 = 1, \alpha = 0 \tag{9.32}$$

$|\chi\rangle$ is an eigenket of S_z with eigenvalue $-\hbar/2$.

- What is $|\chi\rangle$ if it is an eigenket of $\hat{\mathbf{n}} \cdot \mathbf{S}$?

FIXME: F1: standard spherical projection picture, with $\hat{\mathbf{n}}$ projected down onto the x, y plane at angle ϕ and at an angle θ from the z axis.

The eigenvalues will still be $\pm\hbar/2$ since there is nothing special about the z direction.

$$\begin{aligned}\hat{\mathbf{n}} \cdot \mathbf{S} &= n_x S_x + n_y S_y + n_z S_z \\ &\to \frac{\hbar}{2}\begin{bmatrix} n_z & n_x - in_y \\ n_x + in_y & -n_z \end{bmatrix} \\ &= \frac{\hbar}{2}\begin{bmatrix}\cos\theta & \sin\theta e^{-i\phi} \sin\theta e^{i\phi} & -\cos\theta\end{bmatrix}\end{aligned} \tag{9.33}$$

To find the eigenkets we diagonalize this, and we find representations of the eigenkets are

$$|\hat{\mathbf{n}}+\rangle \to \begin{bmatrix}\cos\left(\frac{\theta}{2}\right) e^{-i\phi/2} \\ \sin\left(\frac{\theta}{2}\right) e^{i\phi/2}\end{bmatrix} \tag{9.34}$$

$$|\hat{\mathbf{n}}-\rangle \to \begin{bmatrix}-\sin\left(\frac{\theta}{2}\right) e^{-i\phi/2} \\ \cos\left(\frac{\theta}{2}\right) e^{i\phi/2}\end{bmatrix}, \tag{9.35}$$

with eigenvalues $\hbar/2$ and $-\hbar/2$ respectively.
So in the abstract notation, tossing the specific representation, we have

$$|\hat{\mathbf{n}}+\rangle \rightarrow \cos\left(\frac{\theta}{2}\right) e^{-i\phi/2} |+\rangle \sin\left(\frac{\theta}{2}\right) e^{i\phi/2} |-\rangle \tag{9.36}$$

$$|\hat{\mathbf{n}}-\rangle \rightarrow -\sin\left(\frac{\theta}{2}\right) e^{-i\phi/2} |+\rangle \cos\left(\frac{\theta}{2}\right) e^{i\phi/2} |-\rangle \tag{9.37}$$

9.2 REPRESENTATION OF TWO STATE KETS

Every ket

$$|\chi\rangle \rightarrow \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \tag{9.38}$$

for which

$$|\alpha|^2 + |\beta|^2 = 1 \tag{9.39}$$

can be written in the form eq. (9.34) for some θ and ϕ, neglecting an overall phase factor.
For any ket in H_s, that ket is "spin up" in some direction.
FIXME: show this.

9.3 PAULI SPIN MATRICES

It is useful to write

$$S_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \equiv \frac{\hbar}{2} \sigma_x \tag{9.40}$$

$$S_y = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \equiv \frac{\hbar}{2} \sigma_y \tag{9.41}$$

$$= \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \equiv \frac{\hbar}{2} \sigma_z \tag{9.42}$$

where

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \tag{9.43}$$

$$\sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \tag{9.44}$$

$$\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{9.45}$$

These are the Pauli spin matrices.

Interesting properties

- $$[\sigma_i, \sigma_j] = \sigma_i\sigma_j + \sigma_j\sigma_i = 0, \qquad \text{if } i < j \tag{9.46}$$

- $$\sigma_x\sigma_y = i\sigma_z \tag{9.47}$$

  (and cyclic permutations)

- $$\text{tr}(\sigma_i) = 0 \tag{9.48}$$

- $$(\hat{\mathbf{n}} \cdot \boldsymbol{\sigma})^2 = \sigma_0 \tag{9.49}$$

  where

  $$\hat{\mathbf{n}} \cdot \boldsymbol{\sigma} \equiv n_x\sigma_x + n_y\sigma_y + n_z\sigma_z, \tag{9.50}$$

  and

  $$\sigma_0 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{9.51}$$

  (note $\text{tr}(\sigma_0) \neq 0$)

- $$[\sigma_i, \sigma_j] = 2\delta_{ij}\sigma_0 \tag{9.52}$$
$$[\sigma_x, \sigma_y] = 2i\sigma_z \tag{9.53}$$

  (and cyclic permutations of the latter).

  Can combine these to show that

$$(\mathbf{A}\cdot\boldsymbol{\sigma})(\mathbf{B}\cdot\boldsymbol{\sigma}) = (\mathbf{A}\cdot\mathbf{B})\sigma_0 + i(\mathbf{A}\times\mathbf{B})\cdot\boldsymbol{\sigma} \tag{9.54}$$

  where $\mathbf{A}$ and $\mathbf{B}$ are vectors (or more generally operators that commute with the $\boldsymbol{\sigma}$ matrices).

- $$\mathrm{tr}(\sigma_i\sigma_j) = 2\delta_{ij} \tag{9.55}$$

- $$\mathrm{tr}(\sigma_\alpha\sigma_\beta) = 2\delta_{\alpha\beta}, \tag{9.56}$$

  where $\alpha, \beta = 0, x, y, z$

Note that any complex matrix M can be written as

$$\begin{aligned} M &= \sum_\alpha m_a\sigma_\alpha \\ &= \begin{bmatrix} m_0 + m_z & m_x - im_y \\ m_x + im_y & m_0 - m_z \end{bmatrix} \end{aligned} \tag{9.57}$$

for any four complex numbers m_0, m_x, m_y, m_z
where

$$m_\beta = \frac{1}{2}\,\mathrm{tr}(M\sigma_\beta). \tag{9.58}$$

10

ROTATION OPERATOR IN SPIN SPACE

10.1 FORMAL TAYLOR SERIES EXPANSION

READING: §27.5 in the text [4].

We can formally expand our rotation operator in Taylor series

$$e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{S}/\hbar} = I + (-i\theta\hat{\mathbf{n}}\cdot\mathbf{S}/\hbar) + \frac{1}{2!}(-i\theta\hat{\mathbf{n}}\cdot\mathbf{S}/\hbar)^2 + \frac{1}{3!}(-i\theta\hat{\mathbf{n}}\cdot\mathbf{S}/\hbar)^3 + \cdots \tag{10.1}$$

or

$$\begin{aligned} e^{-i\theta\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}/2} &= I + (-i\theta\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}/2) + \frac{1}{2!}(-i\theta\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}/2)^2 + \frac{1}{3!}(-i\theta\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}/2)^3 + \cdots \\ &= \sigma_0 + \left(\frac{-i\theta}{2}\right)(\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}) + \frac{1}{2!}\left(\frac{-i\theta}{2}\right)(\hat{\mathbf{n}}\cdot\boldsymbol{\sigma})^2 + \frac{1}{3!}\left(\frac{-i\theta}{2}\right)(\hat{\mathbf{n}}\cdot\boldsymbol{\sigma})^3 + \cdots \\ &= \sigma_0 + \left(\frac{-i\theta}{2}\right)(\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}) + \frac{1}{2!}\left(\frac{-i\theta}{2}\right)\sigma_0 + \frac{1}{3!}\left(\frac{-i\theta}{2}\right)(\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}) + \cdots \\ &= \sigma_0\left(1 - \frac{1}{2!}\left(\frac{\theta}{2}\right)^2 + \cdots\right) - i(\hat{\mathbf{n}}\cdot\boldsymbol{\sigma})\left(\frac{\theta}{2} - \frac{1}{3!}\left(\frac{\theta}{2}\right)^3 + \cdots\right) \\ &= \cos(\theta/2)\sigma_0 - i\sin(\theta/2)(\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}) \end{aligned} \tag{10.2}$$

where we have used the fact that $(\hat{\mathbf{n}}\cdot\boldsymbol{\sigma})^2 = \sigma_0$.

So our representation of the spin operator is

$$\begin{aligned} e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{S}/\hbar} &\to \cos(\theta/2)\sigma_0 - i\sin(\theta/2)(\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}) \\ &= \cos(\theta/2)\sigma_0 - i\sin(\theta/2)\left(n_x\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix} + n_y\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix} + n_z\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}\right) \\ &= \begin{bmatrix}\cos(\theta/2) - in_z\sin(\theta/2) & -i(n_x - in_y)\sin(\theta/2)\\ -i(n_x + in_y)\sin(\theta/2) & \cos(\theta/2) + in_z\sin(\theta/2)\end{bmatrix} \end{aligned} \tag{10.3}$$

Note that, in particular,

$$e^{-2\pi i\hat{\mathbf{n}}\cdot\mathbf{S}/\hbar} \to \cos\pi\sigma_0 = -\sigma_0 \tag{10.4}$$

This "rotates" the ket, but introduces a phase factor.

Can do this in general for other degrees of spin, for $s = 1/2, 3/2, 5/2, \cdots$.

Unfortunate interjection by me I mentioned the half angle rotation operator that requires a half angle operator sandwich. Prof. Sipe thought I might be talking about a Heisenberg picture representation, where we have something like this in expectation values

$$\left|\psi'\right\rangle = e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}\left|\psi\right\rangle \tag{10.5}$$

so that

$$\left\langle\psi'\right|O\left|\psi'\right\rangle = \left\langle\psi\right|e^{i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}Oe^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}\left|\psi\right\rangle \tag{10.6}$$

However, what I was referring to, was that a general rotation of a vector in a Pauli matrix basis

$$R(\sum a_k\sigma_k) = R(\mathbf{a}\cdot\boldsymbol{\sigma}) \tag{10.7}$$

can be expressed by sandwiching the Pauli vector representation by two half angle rotation operators like our spin 1/2 operators from class today

$$R(\mathbf{a}\cdot\boldsymbol{\sigma}) = e^{-\theta\hat{\mathbf{u}}\cdot\boldsymbol{\sigma}\hat{\mathbf{v}}\cdot\boldsymbol{\sigma}/2}\mathbf{a}\cdot\boldsymbol{\sigma}e^{\theta\hat{\mathbf{u}}\cdot\boldsymbol{\sigma}\hat{\mathbf{v}}\cdot\boldsymbol{\sigma}/2} \tag{10.8}$$

where $\hat{\mathbf{u}}$ and $\hat{\mathbf{v}}$ are two non-colinear orthogonal unit vectors that define the oriented plane that we are rotating in.

For example, rotating in the $x-y$ plane, with $\hat{\mathbf{u}} = \hat{\mathbf{x}}$ and $\hat{\mathbf{v}} = \hat{\mathbf{y}}$, we have

$$R(\mathbf{a}\cdot\boldsymbol{\sigma}) = e^{-\theta\sigma_1\sigma_2/2}(a_1\sigma_1 + a_2\sigma_2 + a_3\sigma_3)e^{\theta\sigma_1\sigma_2/2} \tag{10.9}$$

Observe that these exponentials commute with σ_3, leaving

$$\begin{aligned} R(\mathbf{a}\cdot\boldsymbol{\sigma}) &= (a_1\sigma_1 + a_2\sigma_2)e^{\theta\sigma_1\sigma_2} + a_3\sigma_3 \\ &= (a_1\sigma_1 + a_2\sigma_2)(\cos\theta + \sigma_1\sigma_2\sin\theta) + a_3\sigma_3 \\ &= \sigma_1(a_1\cos\theta - a_2\sin\theta) + \sigma_2(a_2\cos\theta + a_1\sin\theta) + \sigma_3(a_3) \end{aligned} \tag{10.10}$$

yielding our usual coordinate rotation matrix. Expressed in terms of a unit normal to that plane, we form the normal by multiplication with the unit spatial volume element $I = \sigma_1\sigma_2\sigma_3$. For example:

$$\sigma_1\sigma_2\sigma_3(\sigma_3) = \sigma_1\sigma_2 \tag{10.11}$$

and can in general write a spatial rotation in a Pauli basis representation as a sandwich of half angle rotation matrix exponentials

$$R(\mathbf{a}\cdot\boldsymbol{\sigma}) = e^{-I\theta(\hat{\mathbf{n}}\cdot\boldsymbol{\sigma})/2}(\mathbf{a}\cdot\boldsymbol{\sigma})e^{I\theta(\hat{\mathbf{n}}\cdot\boldsymbol{\sigma})/2} \tag{10.12}$$

when $\hat{\mathbf{n}}\cdot\mathbf{a} = 0$ we get the complex-number like single sided exponential rotation exponentials (since $\mathbf{a}\cdot\boldsymbol{\sigma}$ commutes with $\mathbf{n}\cdot\boldsymbol{\sigma}$ in that case)

$$R(\mathbf{a}\cdot\boldsymbol{\sigma}) = (\mathbf{a}\cdot\boldsymbol{\sigma})e^{I\theta(\hat{\mathbf{n}}\cdot\boldsymbol{\sigma})} \tag{10.13}$$

I believe it was pointed out in one of [5] or [7] that rotations expressed in terms of half angle Pauli matrices has caused some confusion to students of quantum mechanics, because this 2π "rotation" only generates half of the full spatial rotation. It was argued that this sort of confusion can be avoided if one observes that these half angle rotations exponentials are exactly what we require for general spatial rotations, and that a pair of half angle operators are required to produce a full spatial rotation.

The book [5] takes this a lot further, and produces a formulation of spin operators that is devoid of the normal scalar imaginary i (using the Clifford algebra spatial unit volume element instead), and also does not assume a specific matrix representation of the spin operators. They argue that this leads to some subtleties associated with interpretation, but at the time I was attempting to read that text I did know enough QM to appreciate what they were doing, and have not had time to attempt a new study of that content.

Asked about this offline, our Professor says, "Yes.... but I think this kind of result is essentially what I was saying about the 'rotation of operators' in lecture. As to 'interpreting' the -1, there are a number of different strategies and ways of thinking about things. But I think the fact remains that a 2π rotation of a spinor replaces the spinor by -1 times itself, no matter how you formulate things."

That this double sided half angle construction to rotate a vector falls out of the Heisenberg picture is interesting. Even in a purely geometric Clifford algebra context, I suppose that a vector can be viewed as an operator (acting on another vector it produces a scalar and a bivector, acting on higher grade algebraic elements one gets $+1$, -1 grade elements as a result). Yet that is something that is true, independent of any quantum mechanics. In the books I mentioned, this was not derived, but instead stated, and then proved. That is something that I think deserves a bit of exploration. Perhaps there is a more natural derivation possible using infinitesimal arguments ... I had guess that scalar or grade selection would take the place of an expectation value in such a geometric argument.

10.2 SPIN DYNAMICS

At least classically, the angular momentum of charged objects is associated with a magnetic moment as illustrated in fig. 10.1

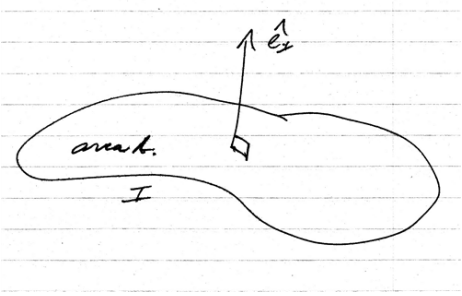

Figure 10.1: Magnetic moment due to steady state current

$$\boldsymbol{\mu} = IA\mathbf{e}_\perp \tag{10.14}$$

In our scheme, following the (cgs?) text conventions of [4], where the **E** and **B** have the same units, we write

$$\boldsymbol{\mu} = \frac{IA}{c}\mathbf{e}_\perp \tag{10.15}$$

For a charge moving in a circle as in fig. 10.2

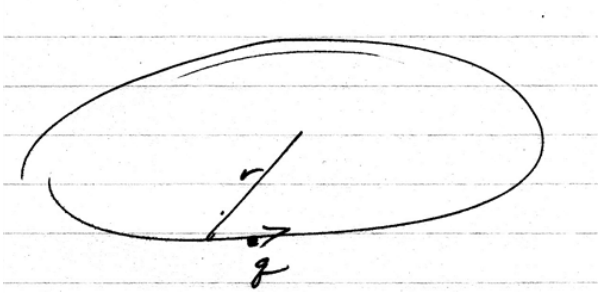

Figure 10.2: Charge moving in circle

$$\begin{aligned} I &= \frac{\text{charge}}{\text{time}} \\ &= \frac{\text{distance}}{\text{time}} \frac{\text{charge}}{\text{distance}} \\ &= \frac{qv}{2\pi r} \end{aligned} \tag{10.16}$$

so the magnetic moment is

$$\begin{aligned} \mu &= \frac{qv}{2\pi r} \frac{\pi r^2}{c} \\ &= \frac{q}{2mc}(mvr) \\ &= \gamma L \end{aligned} \tag{10.17}$$

Here γ is the gyromagnetic ratio
Recall that we have a torque, as shown in fig. 10.3

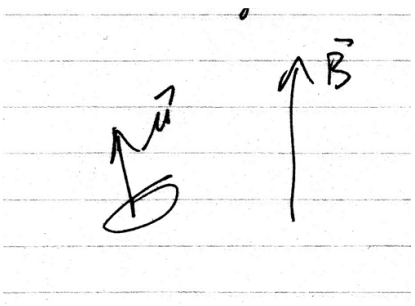

Figure 10.3: Induced torque in the presence of a magnetic field

$$\mathbf{T} = \boldsymbol{\mu} \times \mathbf{B} \tag{10.18}$$

tending to line up $\boldsymbol{\mu}$ with $\mathbf{B}$. The energy is then

$$-\boldsymbol{\mu} \cdot \mathbf{B} \tag{10.19}$$

Also recall that this torque leads to precession as shown in fig. 10.4

$$\frac{d\mathbf{L}}{dt} = \mathbf{T} = \gamma \mathbf{L} \times \mathbf{B}, \tag{10.20}$$

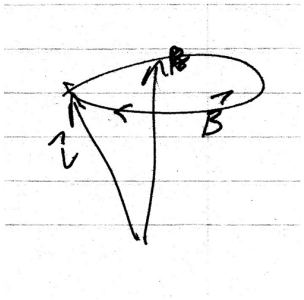

Figure 10.4: Precession due to torque

with precession frequency

$$\boldsymbol{\omega} = -\gamma \mathbf{B}. \tag{10.21}$$

For a current due to a moving electron

$$\gamma = -\frac{e}{2mc} < 0 \tag{10.22}$$

where we are, here, writing for charge on the electron $-e$.

Question: steady state currents only? . Yes, this is only true for steady state currents.

For the translational motion of an electron, even if it is not moving in a steady way, regardless of its dynamics

$$\boldsymbol{\mu}_0 = -\frac{e}{2mc}\mathbf{L} \tag{10.23}$$

Now, back to quantum mechanics, we turn $\boldsymbol{\mu}_0$ into a dipole moment operator and $\mathbf{L}$ is "promoted" to an angular momentum operator.

$$H_{\text{int}} = -\boldsymbol{\mu}_0 \cdot \mathbf{B} \tag{10.24}$$

What about the "spin"?

Perhaps

$$\boldsymbol{\mu}_s = \gamma_s \mathbf{S} \tag{10.25}$$

we write this as

$$\boldsymbol{\mu}_s = g\left(-\frac{e}{2mc}\right)\mathbf{S} \tag{10.26}$$

so that

$$\gamma_s = -\frac{ge}{2mc} \tag{10.27}$$

Experimentally, one finds to very good approximation

$$g = 2 \tag{10.28}$$

There was a lot of trouble with this in early quantum mechanics where people got things wrong, and canceled the wrong factors of 2.

In fact, Dirac's relativistic theory for the electron predicts $g = 2$.

When this is measured experimentally, one does not get exactly $g = 2$, and a theory that also incorporates photon creation and destruction and the interaction with the electron with such (virtual) photons. We get

$$\begin{aligned} g_{\text{theory}} &= 2\left(1.001159652140(\pm 28)\right) \\ g_{\text{experimental}} &= 2\left(1.0011596521884(\pm 43)\right) \end{aligned} \tag{10.29}$$

Richard Feynman compared the precision of quantum mechanics, referring to this measurement, "to predicting a distance as great as the width of North America to an accuracy of one human hair's breadth".

10.3 THE HYDROGEN ATOM WITH SPIN

READING: what chapter of [4] ?

For a spinless hydrogen atom, the Hamiltonian was

$$H = H_{\text{CM}} \otimes H_{\text{rel}} \tag{10.30}$$

where we have independent Hamiltonian's for the motion of the center of mass and the relative motion of the electron to the proton.

The basis kets for these could be designated $|\mathbf{p}_{\text{CM}}\rangle$ and $|\mathbf{p}_{\text{rel}}\rangle$ respectively.

Now we want to augment this, treating

$$H = H_{\text{CM}} \otimes H_{\text{rel}} \otimes H_{\text{s}} \tag{10.31}$$

where H_{s} is the Hamiltonian for the spin of the electron. We are neglecting the spin of the proton, but that could also be included (this turns out to be a lesser effect).

We will introduce a Hamiltonian including the dynamics of the relative motion and the electron spin

$$H_{\text{rel}} \otimes H_{\text{s}} \tag{10.32}$$

Covering the Hilbert space for this system we will use basis kets

$$|nlm\pm\rangle \tag{10.33}$$

$$\begin{aligned} |nlm+\rangle &\rightarrow \begin{bmatrix} \langle \mathbf{r}+|nlm+\rangle \\ \langle \mathbf{r}-|nlm+\rangle \end{bmatrix} = \begin{bmatrix} \Phi_{nlm}(\mathbf{r}) \\ 0 \end{bmatrix} \\ |nlm-\rangle &\rightarrow \begin{bmatrix} \langle \mathbf{r}+|nlm-\rangle \\ \langle \mathbf{r}-|nlm-\rangle \end{bmatrix} = \begin{bmatrix} 0 \\ \Phi_{nlm}(\mathbf{r}) \end{bmatrix}. \end{aligned} \tag{10.34}$$

Here $\mathbf{r}$ should be understood to really mean $\mathbf{r}_{\text{rel}}$. Our full Hamiltonian, after introducing a magnetic pertubation is

$$H = \frac{P_{\text{CM}}^2}{2M} + \left(\frac{P_{\text{rel}}^2}{2\mu} - \frac{e^2}{R_{\text{rel}}} \right) - \boldsymbol{\mu}_0 \cdot \mathbf{B} - \boldsymbol{\mu}_s \cdot \mathbf{B} \tag{10.35}$$

where

$$M = m_{\text{proton}} + m_{\text{electron}}, \tag{10.36}$$

and

$$\frac{1}{\mu} = \frac{1}{m_{\text{proton}}} + \frac{1}{m_{\text{electron}}}. \tag{10.37}$$

For a uniform magnetic field

$$\boldsymbol{\mu}_0 = \left(-\frac{e}{2mc}\right)\mathbf{L} \tag{10.38}$$

$$\boldsymbol{\mu}_s = g\left(-\frac{e}{2mc}\right)\mathbf{S} \tag{10.39}$$

We also have higher order terms (higher order multipoles) and relativistic corrections (like spin orbit coupling [17]).

11

TWO SPIN SYSTEMS, ANGULAR MOMENTUM, AND CLEBSCH-GORDON CONVENTION

11.1 TWO SPINS

READING: §28 of [4].

Example : Consider two electrons, 1 in each of 2 quantum dots.

$$H = H_1 \otimes H_2 \tag{11.1}$$

where H_1 and H_2 are both spin Hamiltonian's for respective 2D Hilbert spaces. Our complete Hilbert space is thus a 4D space.

We will write

$$\begin{aligned} |+\rangle_1 \otimes |+\rangle_2 &= |++\rangle \\ |+\rangle_1 \otimes |-\rangle_2 &= |+-\rangle \\ |-\rangle_1 \otimes |+\rangle_2 &= |-+\rangle \\ |-\rangle_1 \otimes |-\rangle_2 &= |--\rangle \end{aligned} \tag{11.2}$$

Can introduce

$$\begin{aligned} \mathbf{S}_1 &= \mathbf{S}_1^{(1)} \otimes I^{(2)} \\ \mathbf{S}_2 &= I^{(1)} \otimes \mathbf{S}_2^{(2)} \end{aligned} \tag{11.3}$$

Here we "promote" each of the individual spin operators to spin operators in the complete Hilbert space.

We write

$$\begin{aligned} S_{1z}|++\rangle &= \frac{\hbar}{2}|++\rangle \\ S_{1z}|+-\rangle &= \frac{\hbar}{2}|+-\rangle \end{aligned} \tag{11.4}$$

Write

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2, \tag{11.5}$$

for the full spin angular momentum operator. The z component of this operator is

$$S_z = S_{1z} + S_{2z} \tag{11.6}$$

$$\begin{aligned}
S_z|{+}{+}\rangle &= (S_{1z} + S_{2z})|{+}{+}\rangle = \left(\frac{\hbar}{2} + \frac{\hbar}{2}\right)|{+}{+}\rangle = \hbar|{+}{+}\rangle \\
S_z|{+}{-}\rangle &= (S_{1z} + S_{2z})|{+}{-}\rangle = \left(\frac{\hbar}{2} - \frac{\hbar}{2}\right)|{+}{-}\rangle = 0 \\
S_z|{-}{+}\rangle &= (S_{1z} + S_{2z})|{-}{+}\rangle = \left(-\frac{\hbar}{2} + \frac{\hbar}{2}\right)|{-}{+}\rangle = 0 \\
S_z|{-}{-}\rangle &= (S_{1z} + S_{2z})|{-}{-}\rangle = \left(-\frac{\hbar}{2} - \frac{\hbar}{2}\right)|{-}{-}\rangle = -\hbar|{-}{-}\rangle
\end{aligned} \tag{11.7}$$

So, we find that $|xx\rangle$ are all eigenkets of S_z. These will also all be eigenkets of $\mathbf{S}_1^2 = S_{1x}^2 + S_{1y}^2 + S_{1z}^2$ since we have

$$\begin{aligned}
S_1^2|xx\rangle &= \hbar^2\left(\frac{1}{2}\right)\left(1 + \frac{1}{2}\right)|xx\rangle = \frac{3}{4}\hbar^2|xx\rangle \\
S_2^2|xx\rangle &= \hbar^2\left(\frac{1}{2}\right)\left(1 + \frac{1}{2}\right)|xx\rangle = \frac{3}{4}\hbar^2|xx\rangle
\end{aligned} \tag{11.8}$$

$$\begin{aligned}
S^2 &= (\mathbf{S}_1 + \mathbf{S}_2)\cdot(\mathbf{S}_1 + \mathbf{S}_2) \\
&= S_1^2 + S_2^2 + 2\mathbf{S}_1\cdot\mathbf{S}_2
\end{aligned} \tag{11.9}$$

Note that we have a commutation assumption here $[S_{1i}, S_{2i}] = 0$, since we have written $2\mathbf{S}_1\cdot\mathbf{S}_2$ instead of $\sum_i S_{1i}S_{2i} + S_{2i}S_{1i}$. The justification for this appears to be the promotion of the spin operators in eq. (11.3) to operators in the complete Hilbert space, since each of these spin operators acts only on the kets associated with their index.

Are all the product kets also eigenkets of S^2? Calculate

$$\begin{aligned}
S^2|{+}{-}\rangle &= (S_1^2 + S_2^2 + 2\mathbf{S}_1\cdot\mathbf{S}_2)|{+}{-}\rangle \\
&= \left(\frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2\right) + 2S_{1x}S_{2x}|{+}{-}\rangle + 2S_{1y}S_{2y}|{+}{-}\rangle + 2S_{1z}S_{2z}|{+}{-}\rangle
\end{aligned} \tag{11.10}$$

For the z mixed terms, we have

$$2S_{1z}S_{2z}|+-\rangle = 2\left(\frac{\hbar}{2}\right)\left(-\frac{\hbar}{2}\right)|+-\rangle \tag{11.11}$$

So

$$S^2|+-\rangle = \hbar^2|+-\rangle + 2S_{1x}S_{2x}|+-\rangle + 2S_{1y}S_{2y}|+-\rangle \tag{11.12}$$

Since we have set our spin direction in the z direction with

$$\begin{aligned} |+\rangle &\rightarrow \begin{bmatrix} 1 \\ 0 \end{bmatrix} \\ |-\rangle &\rightarrow \begin{bmatrix} 0 \\ 1 \end{bmatrix} \end{aligned} \tag{11.13}$$

We have

$$\begin{aligned} S_x|+\rangle &\rightarrow \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{\hbar}{2}|-\rangle \\ S_x|-\rangle &\rightarrow \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{\hbar}{2}|+\rangle \\ S_y|+\rangle &\rightarrow \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{i\hbar}{2}\begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{i\hbar}{2}|-\rangle \\ S_y|-\rangle &\rightarrow \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{-i\hbar}{2}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = -\frac{i\hbar}{2}|+\rangle \end{aligned} \tag{11.14}$$

And are able to arrive at the action of S^2 on our mixed composite state

$$S^2|+-\rangle = \hbar^2(|+-\rangle + |-+\rangle). \tag{11.15}$$

For the action on the $|++\rangle$ state we have

$$\begin{aligned} S^2|++\rangle &= \left(\frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2\right)|++\rangle + 2\frac{\hbar^2}{4}|--\rangle + 2i^2\frac{\hbar^2}{4}|--\rangle + 2\left(\frac{\hbar}{2}\right)\left(\frac{\hbar}{2}\right)|++\rangle \\ &= 2\hbar^2|++\rangle \end{aligned} \tag{11.16}$$

and on the $|--\rangle$ state we have

$$\begin{aligned} S^2|--\rangle &= \left(\frac{3}{4}\hbar^2+\frac{3}{4}\hbar^2\right)|--\rangle + 2\frac{(-\hbar)^2}{4}|++\rangle + 2i^2\frac{\hbar^2}{4}|++\rangle + 2\left(-\frac{\hbar}{2}\right)\left(-\frac{\hbar}{2}\right)|--\rangle \\ &= 2\hbar^2|--\rangle \end{aligned} \tag{11.17}$$

All of this can be assembled into a tidier matrix form

$$S^2 \to \hbar^2\begin{bmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{bmatrix}, \tag{11.18}$$

where the matrix is taken with respect to the (ordered) basis

$$\{|++\rangle, |+-\rangle, |-+\rangle, |--\rangle\}. \tag{11.19}$$

However,

$$\begin{aligned} \left[S^2, S_z\right] &= 0 \\ \left[S_i, S_j\right] &= i\hbar\sum_k \epsilon_{ijk}S_k \end{aligned} \tag{11.20}$$

(Also, $\left[S^2, S_i\right] = 0$.)
It should be possible to find eigenkets of S^2 and S_z

$$\begin{aligned} S^2|sm_s\rangle &= s(s+1)\hbar^2|sm_s\rangle \\ S_z|sm_s\rangle &= \hbar m_s|sm_s\rangle \end{aligned} \tag{11.21}$$

An orthonormal set of eigenkets of S^2 and S_z is found to be

$$\begin{array}{ll} |++\rangle & s=1 \text{ and } m_s=1 \\ \frac{1}{\sqrt{2}}\left(|+-\rangle + |-+\rangle\right) & s=1 \text{ and } m_s=0 \\ |--\rangle & s=1 \text{ and } m_s=-1 \\ \frac{1}{\sqrt{2}}\left(|+-\rangle - |-+\rangle\right) & s=0 \text{ and } m_s=0 \end{array} \tag{11.22}$$

The first three kets here can be grouped into a triplet in a 3D Hilbert space, whereas the last treated as a singlet in a 1D Hilbert space.

Form a grouping

$$H = H_1 \otimes H_2 \tag{11.23}$$

Can write

$$\frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0 \tag{11.24}$$

where the 1 and 0 here refer to the spin index s.

Other examples Consider, perhaps, the $l = 5$ state of the hydrogen atom

$$\begin{aligned} J_1^2 |j_1 m_1\rangle &= j_1(j_1+1)\hbar^2 |j_1 m_1\rangle \\ J_{1z} |j_1 m_1\rangle &= \hbar m_1 |j_1 m_1\rangle \end{aligned} \tag{11.25}$$

$$\begin{aligned} J_2^2 |j_2 m_2\rangle &= j_2(j_2+1)\hbar^2 |j_2 m_2\rangle \\ J_{2z} |j_2 m_2\rangle &= \hbar m_2 |j_2 m_2\rangle \end{aligned} \tag{11.26}$$

Consider the Hilbert space spanned by $|j_1 m_1\rangle \otimes |j_2 m_2\rangle$, a $(2j_1+1)(2j_2+1)$ dimensional space. How to find the eigenkets of J^2 and J_z?

11.2 MORE ON TWO SPIN SYSTEMS

READING: Covering §26.5 of the text [4].

$$\frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0 \tag{11.27}$$

where 1 is a triplet state for $s = 1$ and 0 the "singlet" state with $s = 0$. We want to consider the angular momentum of the entire system

$$j_1 \otimes j_2 = ? \tag{11.28}$$

Why bother? Often it is true that

$$[H, \mathbf{J}] = 0, \tag{11.29}$$

so, in that case, the eigenstates of the total angular momentum are also energy eigenstates, so considering the angular momentum problem can help in finding these energy eigenstates.

Rotation operator

$$e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar} \tag{11.30}$$

$$\hat{\mathbf{n}}\cdot\mathbf{J} = n_x J_x + n_y J_y + n_z J_z \tag{11.31}$$

Recall the definitions of the raising or lowering operators

$$J_\pm = J_x \pm iJ_y, \tag{11.32}$$

or

$$\begin{aligned} J_x &= \frac{1}{2}(J_+ + J_-) \\ J_y &= \frac{1}{2i}(J_+ - J_-) \end{aligned} \tag{11.33}$$

We have

$$\hat{\mathbf{n}}\cdot\mathbf{J} = n_x\frac{1}{2}(J_+ + J_-) + n_y\frac{1}{2i}(J_+ - J_-) + n_z J_z, \tag{11.34}$$

and

$$J_\pm\,|jm\rangle = \hbar\big((j\mp m)(j\pm m_1)\big)^{1/2}\,|j,m\pm 1\rangle \tag{11.35}$$

So

$$\langle j'm'|\, e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}\,|jm\rangle = 0 \tag{11.36}$$

unless $j = j'$.

$$\langle jm'|\, e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}\,|jm\rangle \tag{11.37}$$

is a $(2j+1)\times(2j+1)$ matrix.
Combining rotations

$$\langle jm'|\, e^{-i\theta_b\hat{\mathbf{n}}_a\cdot\mathbf{J}/\hbar}e^{-i\theta_a\hat{\mathbf{n}}_b\cdot\mathbf{J}/\hbar}\,|jm\rangle = \sum_{m''}\langle jm'|\, e^{-i\theta_b\hat{\mathbf{n}}_a\cdot\mathbf{J}/\hbar}\,|jm''\rangle\langle jm''|\, e^{-i\theta_a\hat{\mathbf{n}}_b\cdot\mathbf{J}/\hbar}\,|jm\rangle \tag{11.38}$$

If

$$e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar} = e^{-i\theta_b\hat{\mathbf{n}}_a\cdot\mathbf{J}/\hbar}e^{-i\theta_a\hat{\mathbf{n}}_b\cdot\mathbf{J}/\hbar} \tag{11.39}$$

(something that may be hard to compute but possible), then

$$\langle jm'|\, e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}\,|jm\rangle = \sum_{m''}\langle jm'|\, e^{-i\theta_b\hat{\mathbf{n}}_a\cdot\mathbf{J}/\hbar}\,|jm''\rangle\langle jm''|\, e^{-i\theta_a\hat{\mathbf{n}}_b\cdot\mathbf{J}/\hbar}\,|jm\rangle \tag{11.40}$$

For fixed j, the matrices $\langle jm'|\, e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}\,|jm\rangle$ form a representation of the rotation group. The $(2j+1)$ representations are irreducible. (This will not be proven).

It may be that there may be big blocks of zeros in some of the matrices, but they cannot be simplified any further?

Back to the two particle system

$$j_1 \otimes j_2 = ? \tag{11.41}$$

If we use

$$|j_1 m_1\rangle \otimes |j_2 m_2\rangle \tag{11.42}$$

If a j_1 and a j_2 are picked then

$$\langle j_1 m_1'; j_2 m_2'|\, e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}\,|j_1 m_1; j_2 m_2\rangle \tag{11.43}$$

is also a representation of the rotation group, but these sort of matrices can be simplified a lot. This basis of dimensionality $(2j_1+1)(2j_2+1)$ is reducible.

A lot of this is motivation, and we still want a representation of $j_1 \otimes j_2$.

Recall that

$$\frac{1}{2}\otimes\frac{1}{2} = 1\oplus 0 = \left(\frac{1}{2}+\frac{1}{2}\right)\oplus\left(\frac{1}{2}-\frac{1}{2}\right) \tag{11.44}$$

Might guess that, for $j_1 \geq j_2$

$$j_1 \otimes j_2 = (j_1+j_2)\oplus(j_1+j_2-1)\oplus\cdots(j_1-j_2) \tag{11.45}$$

Suppose that this is right. Then

$$5\otimes\frac{1}{2} = \frac{11}{2}\oplus\frac{9}{2} \tag{11.46}$$

Check for dimensions.

$$\begin{aligned} 1 \otimes 1 &= 2 \oplus 1 \oplus 0 \\ 3 \times 3 &= 5 + 3 + 1 \end{aligned} \tag{11.47}$$

Q : What was this $\oplus$?

It was just made up. We are creating a shorthand to say that we have a number of different basis states for each of the groupings. I Need an example!

Check for dimensions in general

$$(2j_1 + 1)(2j_2 + 1) \stackrel{?}{=} \tag{11.48}$$

We find

$$\begin{aligned} \sum_{j_1 - j_2}^{j_1 + j_2} (2j + 1) &= \sum_{j=0}^{j_1 + j_2} (2j + 1) - \sum_{j=0}^{j_1 - j_2 - 1} (2j + 1) \\ &= (2j_1 + 1)(2j_2 + 1) \end{aligned} \tag{11.49}$$

Using

$$\sum_{n=0}^{N} n = \frac{N(N+1)}{2} \tag{11.50}$$

$$j_1 \otimes j_2 = (j_1 + j_2) \oplus (j_1 + j_2 - 1) \oplus \cdots (j_1 - j_2) \tag{11.51}$$

In fact, this is correct. Proof "by construction" to follow.

$$|j_1 m_1\rangle \otimes |j_2 m_2\rangle \tag{11.52}$$

$$\begin{aligned} J^2 |jm\rangle &= j(j+1)\hbar^2 |jm\rangle \\ J_z |jm\rangle &= m\hbar |jm\rangle \end{aligned} \tag{11.53}$$

denote also by

$$|jm; j_1 j_2\rangle\,, \tag{11.54}$$

but will often omit the ; $j_1 j_2$ portion.
With

$j =$	$j_1 + j_2$	$j_1 + j_2 - 1$	$\cdots$	$j_1 - j_2$
	$\lvert j_1 + j_2, j_1 + j_2\rangle$			
	$\lvert j_1 + j_2, j_1 + j_2 - 1\rangle$	$\lvert j_1 + j_2 - 1, j_1 + j_2 - 1\rangle$		
		$\lvert j_1 + j_2 - 1, j_1 + j_2 - 2\rangle$		
	$\vdots$			$\lvert j_1 - j_2, j_1 - j_2\rangle$
	$\vdots$			$\vdots$
	$\vdots$			$\lvert j_1 - j_2, -(j_1 - j_2)\rangle$
	$\vdots$			
	$\lvert j_1 + j_2, -(j_1 + j_2 - 1)\rangle$	$\lvert j_1 + j_2 - 1, -(j_1 + j_2 - 1)\rangle$		
	$\lvert j_1 + j_2, -(j_1 + j_2)\rangle$			

(11.55)

Look at

$$|j_1 + j_2, j_1 + j_2\rangle \tag{11.56}$$

$$J_z\,|j_1 + j_2, j_1 + j_2\rangle = (j_1 + j_2)\,\hbar\,|j_1 + j_2, j_1 + j_2\rangle \tag{11.57}$$

$$J_z(|j_1 m_1\rangle \otimes |j_2 m_2\rangle) = (m_1 + m_2)\,\hbar(|j_1 m_1\rangle \otimes |j_2 m_2\rangle) \tag{11.58}$$

we must have

$$|j_1 + j_2, j_1 + j_2\rangle = e^{i\phi}(|j_1 j_1\rangle \otimes |j_2 j_2\rangle) \tag{11.59}$$

So $|j_1 + j_2, j_1 + j_2\rangle$ must be a superposition of states $|j_1 m_1\rangle \otimes |j_2 m_2\rangle$ with $m_1 + m_2 = j_1 + j_2$. Choosing $e^{i\phi} = 1$ is called the Clebsch-Gordan convention.

$$|j_1 + j_2, j_1 + j_2\rangle = |j_1 j_1\rangle \otimes |j_2 j_2\rangle \tag{11.60}$$

We now move down column.

$$J_- |j_1 + j_2, j_1 + j_2\rangle = \hbar(2(j_1 + j_2))^{1/2} |j_1 + j_2, j_1 + j_2 - 1\rangle \tag{11.61}$$

So

$$\begin{aligned} |j_1 + j_2, j_1 + j_2 - 1\rangle &= \frac{J_- |j_1 + j_2, j_1 + j_2\rangle}{\hbar(2(j_1 + j_2))^{1/2}} \\ &= \frac{(J_{1-} + J_{2-}) |j_1 j_1\rangle \otimes |j_2 j_2\rangle}{\hbar(2(j_1 + j_2))^{1/2}} \end{aligned} \tag{11.62}$$

11.3 RECAP: TABLE OF TWO SPIN ANGULAR MOMENTA

Recall our table

$j =$	$j_1 + j_2$	$j_1 + j_2 - 1$	$\cdots$	$j_1 - j_2$
	$\|j_1 + j_2, j_1 + j_2\rangle$			
	$\|j_1 + j_2, j_1 + j_2 - 1\rangle$	$\|j_1 + j_2 - 1, j_1 + j_2 - 1\rangle$		
		$\|j_1 + j_2 - 1, j_1 + j_2 - 2\rangle$		
	$\vdots$			$\|j_1 - j_2, j_1 - j_2\rangle$
	$\vdots$			$\vdots$
	$\vdots$			$\|j_1 - j_2, -(j_1 - j_2)\rangle$
	$\vdots$			
	$\|j_1 + j_2, -(j_1 + j_2 - 1)\rangle$	$\|j_1 + j_2 - 1, -(j_1 + j_2 - 1)\rangle$		
	$\|j_1 + j_2, -(j_1 + j_2)\rangle$			

(11.63)

First column Let us start with computation of the kets in the lowest position of the first column, which we will obtain by successive application of the lowering operator to the state

$$|j_1 + j_2, j_1 + j_2\rangle = |j_1 j_1\rangle \otimes |j_2 j_2\rangle \,. \tag{11.64}$$

Recall that our lowering operator was found to be (or defined as)

$$J_- |j, m\rangle = \sqrt{(j + m)(j - m + 1)}\, \hbar\, |j, m - 1\rangle \,, \tag{11.65}$$

so that application of the lowering operator gives us

$$\begin{aligned}
|j_1 + j_2, j_1 + j_2 - 1\rangle &= \frac{J_- |j_1 j_1\rangle \otimes |j_2 j_2\rangle}{(2(j_1 + j_2))^{1/2}\,\hbar} \\
&= \frac{(J_{1-} + J_{2-}) |j_1 j_1\rangle \otimes |j_2 j_2\rangle}{(2(j_1 + j_2))^{1/2}\,\hbar} \\
&= \frac{\left(\sqrt{(j_1 + j_1)(j_1 - j_1 + 1)}\,\hbar\, |j_1(j_1 - 1)\rangle\right) \otimes |j_2 j_2\rangle}{(2(j_1 + j_2))^{1/2}\,\hbar} \\
&\quad + \frac{|j_1 j_1\rangle \otimes \left(\sqrt{(j_2 + j_2)(j_2 - j_2 + 1)}\,\hbar\, |j_2(j_2 - 1)\rangle\right)}{(2(j_1 + j_2))^{1/2}\,\hbar} \\
&= \left(\frac{j_1}{j_1 + j_2}\right)^{1/2} |j_1(j_1 - 1)\rangle \otimes |j_2 j_2\rangle + \left(\frac{j_2}{j_1 + j_2}\right)^{1/2} |j_1 j_1\rangle \otimes |j_2(j_2 - 1)\rangle
\end{aligned} \tag{11.66}$$

Proceeding iteratively would allow us to finish off this column.

Second column Moving on to the second column, the top most element in the table

$$|j_1 + j_2 - 1, j_1 + j_2 - 1\rangle\,, \tag{11.67}$$

can only be made up of $|j_1 m_1\rangle \otimes |j_2 m_2\rangle$ with $m_1 + m_2 = j_1 + j_2 - 1$. There are two possibilities

$$\begin{aligned}
m_1 &= j_1 \qquad m_2 = j_2 - 1 \\
m_1 &= j_1 - 1 \quad m_2 = j_2
\end{aligned} \tag{11.68}$$

So for some A and B to be determined we must have

$$|j_1 + j_2 - 1, j_1 + j_2 - 1\rangle = A\,|j_1 j_1\rangle \otimes |j_2(j_2 - 1)\rangle + B\,|j_1(j_1 - 1)\rangle \otimes |j_2 j_2\rangle \tag{11.69}$$

Observe that these are the same kets that we ended up with by application of the lowering operator on the topmost element of the first column in our table. Since $|j_1 + j_2, j_1 + j_2 - 1\rangle$ and $|j_1 + j_2 - 1, j_1 + j_2 - 1\rangle$ are orthogonal, we can construct our ket for the top of the second column by just seeking such an orthonormal superposition. Consider for example

$$\begin{aligned}
0 &= (a\,\langle b| + c\,\langle d|)(A\,|b\rangle + C\,|d\rangle) \\
&= aA + cC
\end{aligned} \tag{11.70}$$

With $A = 1$ we find that $C = -a/c$, so we have

$$\begin{aligned} A\,|b\rangle + C\,|d\rangle &= |b\rangle - \frac{a}{c}\,|d\rangle \\ &\sim c\,|b\rangle - a\,|d\rangle \end{aligned} \tag{11.71}$$

So we find, for real a and c that

$$0 = (a\,\langle b| + c\,\langle d|)(c\,|b\rangle - a\,|d\rangle), \tag{11.72}$$

for any orthonormal pair of kets $|a\rangle$ and $|d\rangle$. Using this we find

$$|j_1 + j_2 - 1, j_1 + j_2 - 1\rangle = \left(\frac{j_2}{j_1 + j_2}\right)^{1/2} |j_1 j_1\rangle \otimes |j_2(j_2 - 1)\rangle - \left(\frac{j_1}{j_1 + j_2}\right)^{1/2} |j_1(j_1 - 1)\rangle \otimes |j_2 j_2\rangle \tag{11.73}$$

This will work, although we could also multiply by any phase factor if desired. Such a choice of phase factors is essentially just a convention.

The Clebsch-Gordon convention This is the convention we will use, where we

- choose the coefficients to be real.
- require the coefficient of the $m_1 = j_1$ term to be ≥ 0

This gives us the first state in the second column, and we can proceed to iterate using the lowering operators to get all those values.

Moving on to the third column

$$|j_1 + j_2 - 2, j_1 + j_2 - 2\rangle \tag{11.74}$$

can only be made up of $|j_1 m_1\rangle \otimes |j_2 m_2\rangle$ with $m_1 + m_2 = j_1 + j_2 - 2$. There are now three possibilities

$$\begin{aligned} m_1 &= j_1 & m_2 &= j_2 - 2 \\ m_1 &= j_1 - 2 & m_2 &= j_2 \\ m_1 &= j_1 - 1 & m_2 &= j_2 - 1 \end{aligned} \tag{11.75}$$

and 2 orthogonality conditions, plus conventions. This is enough to determine the ket in the third column.

We can formally write

$$|jm; j_1 j_2\rangle = \sum_{m_1,m_2} |j_1 m_1, j_2 m_2\rangle \langle j_1 m_1, j_2 m_2 | jm; j_1 j_2\rangle \tag{11.76}$$

where

$$|j_1 m_1, j_2 m_2\rangle = |j_1 m_1\rangle \otimes |j_2 m_2\rangle\,, \tag{11.77}$$

and

$$\langle j_1 m_1, j_2 m_2 | jm; j_1 j_2\rangle \tag{11.78}$$

are the Clebsch-Gordon coefficients, sometimes written as

$$\langle j_1 m_1, j_2 m_2 | jm\rangle \tag{11.79}$$

Properties

1. $\langle j_1 m_1, j_2 m_2 | jm\rangle \neq 0$ only if $j_1 - j_2 \leq j \leq j_1 + j + 2$

   This is sometimes called the triangle inequality, depicted in fig. 11.1

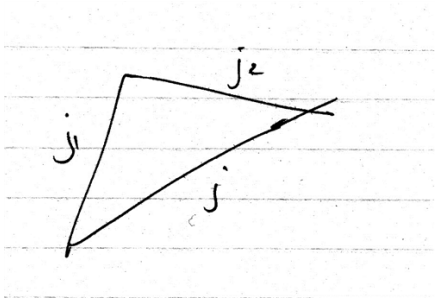

Figure 11.1: Angular momentum triangle inequality

2. $\langle j_1 m_1, j_2 m_2 | jm\rangle \neq 0$ only if $m = m_1 + m_2$.
3. Real (convention).
4. $\langle j_1 j_1, j_2 (j - j_1) | jj\rangle$ positive (convention again).

5. Proved in the text. If follows that

$$\langle j_1 m_1, j_2 m_2 | jm \rangle = (-1)^{j_1+j_2-j} \langle j_1(-m_1), j_2(-m_2) | j(-m) \rangle \tag{11.80}$$

Note that the $\langle j_1 m_1, j_2 m_2 | jm \rangle$ are all real. So, they can be assembled into an orthogonal matrix. Example

$$\begin{bmatrix} |11\rangle \\ |10\rangle \\ \left|\overline{11}\right\rangle \\ |00\rangle \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \\ 0 & \frac{1}{\sqrt{2}} & \frac{-1}{\sqrt{2}} & 0 \end{bmatrix} \begin{bmatrix} |++\rangle \\ |++\rangle \\ |-+\rangle \\ |--\rangle \end{bmatrix} \tag{11.81}$$

Example. Electrons Consider the special case of an electron, a spin 1/2 particle with $s = 1/2$ and $m_s = \pm 1/2$ where we have

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{11.82}$$

$$|lm\rangle \otimes \left|\frac{1}{2} m_s\right\rangle \tag{11.83}$$

possible values of j are $l \pm 1/2$

$$l \otimes \frac{1}{2} = \left(l + \frac{1}{2}\right) \oplus \left(l - \frac{1}{2}\right) \tag{11.84}$$

Our table representation is then

$j =$	$l + \frac{1}{2}$	$l - \frac{1}{2}$
	$\left\|l + \frac{1}{2}, l + \frac{1}{2}\right\rangle$	
	$\left\|l + \frac{1}{2}, l + \frac{1}{2} - 1\right\rangle$	$\left\|l - \frac{1}{2}, l - \frac{1}{2}\right\rangle$
		$\left\|l - \frac{1}{2}, -(l - \frac{1}{2}\right\rangle$
	$\left\|l + \frac{1}{2}, -(l + \frac{1}{2})\right\rangle$	

(11.85)

Here $\left|l+\frac{1}{2},m\right\rangle$
can only have contributions from

$$\left|l,m-\frac{1}{2}\right\rangle\otimes\left|\frac{1}{2}\frac{1}{2}\right\rangle$$
$$\left|l,m+\frac{1}{2}\right\rangle\otimes\left|\frac{1}{2}\frac{\overline{1}}{2}\right\rangle \tag{11.86}$$

$\left|l-\frac{1}{2},m\right\rangle$ from the same two. So using this and conventions we can work out (in §28 page 524, of our text [4]).

$$\begin{aligned}\left|l\pm\frac{1}{2},m\right\rangle = &\pm\frac{1}{\sqrt{2l+1}}(l+\frac{1}{2}\pm m)^{1/2}\left|l,m-\frac{1}{2}\right\rangle\times\left|\frac{1}{2}\frac{1}{2}\right\rangle\\ &\pm\frac{1}{\sqrt{2l+1}}(l+\frac{1}{2}\mp m)^{1/2}\left|l,m+\frac{1}{2}\right\rangle\times\left|\frac{1}{2}\frac{\overline{1}}{2}\right\rangle\end{aligned} \tag{11.87}$$

11.4 TENSOR OPERATORS

§29 of the text.

Recall how we characterized a rotation

$$\mathbf{r}\to\mathcal{R}(\mathbf{r}). \tag{11.88}$$

Here we are using an active rotation as depicted in fig. 11.2

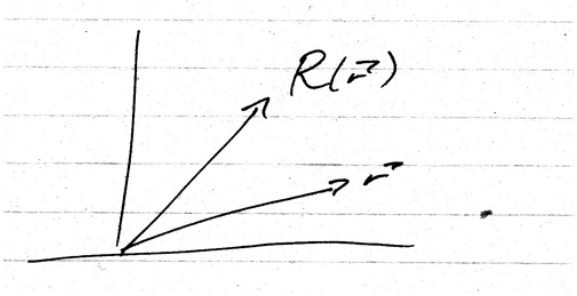

Figure 11.2: active rotation

Suppose that

$$\left[\mathcal{R}(\mathbf{r})\right]_i=\sum_j M_{ij}r_j \tag{11.89}$$

so that

$$U = e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar} \tag{11.90}$$

rotates in the same way. Rotating a ket as in fig. 11.3

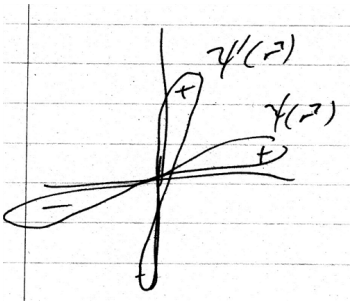

Figure 11.3: Rotating a wavefunction

Rotating a ket

$$|\psi\rangle \tag{11.91}$$

using the prescription

$$|\psi'\rangle = e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}\,|\psi\rangle \tag{11.92}$$

and write

$$|\psi'\rangle = U[M]\,|\psi\rangle \tag{11.93}$$

Now look at

$$\langle\psi|\,O\,|\psi\rangle \tag{11.94}$$

and compare with

$$\langle\psi'|\,O\,|\psi'\rangle = \langle\psi|\,\overbrace{\boxed{U^\dagger[M]OU[M]}}^{(*)}\,|\psi\rangle \tag{11.95}$$

We will be looking in more detail at $(*)$.

12

ROTATIONS OF OPERATORS AND SPHERICAL TENSORS

12.1 SETUP

READING: §28 [4].

Rotating with $U[M]$ as in fig. 12.1

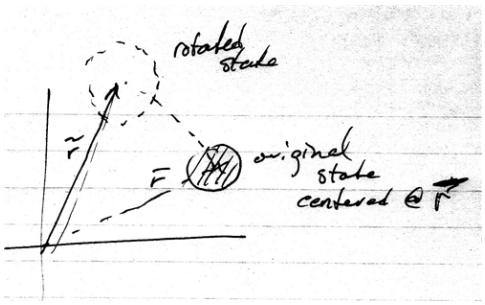

Figure 12.1: Rotating a state centered at F

$$\tilde{r}_i = \sum_j M_{ij} \bar{r}_j \tag{12.1}$$

$$\langle \psi | R_i | \psi \rangle = \bar{r}_i \tag{12.2}$$

$$\begin{aligned} \langle \psi | U^\dagger[M] R_i U[M] | \psi \rangle = \tilde{r}_i &= \sum_j M_{ij} \bar{r}_j \\ &= \langle \psi | \left(U^\dagger[M] R_i U[M] \right) | \psi \rangle \end{aligned} \tag{12.3}$$

So

$$U^\dagger[M] R_i U[M] = \sum_j M_{ij} R_j \tag{12.4}$$

Any three operators V_x, V_y, V_z that transform according to

$$U^\dagger[M]V_i U[M] = \sum_j M_{ij} V_j \tag{12.5}$$

form the components of a vector operator.

12.2 INFINITESIMAL ROTATIONS

Consider infinitesimal rotations, where we can show (problem set 11, problem 1) that

$$\left[V_i, J_j\right] = i\hbar \sum_k \epsilon_{ijk} V_k \tag{12.6}$$

Note that for $V_i = J_i$ we recover the familiar commutator rules for angular momentum, but this also holds for operators **R**, **P**, **J**, ...

Note that

$$U^\dagger[M] = U[M^{-1}] = U[M^{\mathrm{T}}], \tag{12.7}$$

so

$$U^\dagger[M]V_i U^\dagger[M] = U^\dagger[M^\dagger]V_i U[M^\dagger] = \sum_j M_{ji} V_j \tag{12.8}$$

so

$$\langle\psi| V_i |\psi\rangle = \langle\psi| U^\dagger[M]\big(U[M]V_i U^\dagger[M]\big)U[M] |\psi\rangle \tag{12.9}$$

In the same way, suppose we have nine operators

$$\tau_{ij}, \qquad i, j = x, y, z \tag{12.10}$$

that transform according to

$$U[M]\tau_{ij}U^\dagger[M] = \sum_{lm} M_{li} M_{mj} \tau_{lm} \tag{12.11}$$

then we will call these the components of (Cartesian) a second rank tensor operator. Suppose that we have an operator S that transforms

$$U[M]S\,U^{\dagger}[M] = S \tag{12.12}$$

Then we will call S a scalar operator.

12.3 A PROBLEM

This all looks good, but it is really not satisfactory. There is a problem.

Suppose that we have a Cartesian tensor operator like this, lets look at the quantity

$$\begin{aligned}\sum_i \tau_{ii} &= \sum_i U[M]\tau_{ii}U^{\dagger}[M] \\ &= \sum_i \sum_{lm} M_{li}M_{mi}\tau_{lm} \\ &= \sum_i \sum_{lm} M_{li}M^{\mathrm{T}}_{im}\tau_{lm} \\ &= \sum_{lm} \delta_{lm}\tau_{lm} \\ &= \sum_l \tau_{ll}\end{aligned} \tag{12.13}$$

We see buried inside these Cartesian tensors of higher rank there is some simplicity embedded (in this case trace invariance). Who knows what other relationships are also there? We want to work with and extract the buried simplicities, and we will find that the Cartesian way of expressing these tensors is horribly inefficient. What is a representation that does not have any excess information, and is in some sense minimal?

12.4 HOW DO WE EXTRACT THESE BURIED SIMPLICITIES?

Recall

$$U[M]\left|jm''\right\rangle \tag{12.14}$$

gives a linear combination of the $|jm'\rangle$.

$$\begin{aligned} U[M]\left|jm''\right\rangle &= \sum_{m'} \left|jm'\right\rangle \left\langle jm'\right| U[M] \left|jm''\right\rangle \\ &= \sum_{m'} \left|jm'\right\rangle D^{(j)}_{m'm''}[M] \end{aligned} \tag{12.15}$$

We have talked about before how these $D^{(j)}_{m'm''}[M]$ form a representation of the rotation group. These are in fact (not proved here) an irreducible representation.

Look at each element of $D^{(j)}_{m'm''}[M]$. These are matrices and will be different according to which rotation M is chosen. There is some M for which this element is nonzero. There is no element in this matrix element that is zero for all possible M. There are more formal ways to think about this in a group theory context, but this is a physical way to think about this.

Think of these as the basis vectors for some eigenket of J^2.

$$\begin{aligned} |\psi\rangle &= \sum_{m''} \left|jm''\right\rangle \left\langle jm''\right|\psi\rangle \\ &= \sum_{m''} \bar{a}_{m''} \left|jm''\right\rangle \end{aligned} \tag{12.16}$$

where

$$\bar{a}_{m''} = \left\langle jm''\right|\psi\rangle \tag{12.17}$$

So

$$\begin{aligned} U[M]\,|\psi\rangle = &= \sum_{m'} U[M] \left|jm'\right\rangle \left\langle jm'\right|\psi\rangle \\ &= \sum_{m'} U[M] \left|jm'\right\rangle \bar{a}_{m'} \\ &= \sum_{m',m''} \left|jm''\right\rangle \left\langle jm''\right| U[M] \left|jm'\right\rangle \bar{a}_{m'} \\ &= \sum_{m',m''} \left|jm''\right\rangle D^{(j)}_{m'',m'} \bar{a}_{m'} \\ &= \sum_{m''} \tilde{a}_{m''} \left|jm''\right\rangle \end{aligned} \tag{12.18}$$

where

$$\tilde{a}_{m''} = \sum_{m'} D^{(j)}_{m'',m'} \bar{a}_{m'} \tag{12.19}$$

Recall that

$$\tilde{r}_j = \sum_j M_{ij}\bar{r}_j \tag{12.20}$$

Define $(2k+1)$ operators ${T_k}^q$, $q = k, k-1, \cdots -k$ as the elements of a spherical tensor of rank k if

$$U[M]{T_k}^q U^\dagger[M] = \sum_{q'} D^{(j)}_{q'q}{T_k}^{q'} \tag{12.21}$$

Here we are looking for a better way to organize things, and it will turn out (not to be proved) that this will be an irreducible way to represent things.

12.5 MOTIVATING SPHERICAL TENSORS

We want to work though some examples of spherical tensors, and how they relate to Cartesian tensors. To do this, a motivating story needs to be told.

Let us suppose that $|\psi\rangle$ is a ket for a single particle. Perhaps we are talking about an electron without spin, and write

$$\begin{aligned}\langle \mathbf{r}|\psi\rangle &= Y_{lm}(\theta,\phi)f(r)\\ &= \sum_{m''}\bar{a}_{m''}Y_{lm''}(\theta,\phi)\end{aligned} \tag{12.22}$$

for $\bar{a}_{m''} = \delta_{m''m}$ and after dropping $f(r)$. So

$$\langle \mathbf{r}|\, U[M]\,|\psi\rangle = \sum_{m''}\sum_{m'} D^{(j)}_{m''m}\bar{a}_{m'}Y_{lm''}(\theta,\phi) \tag{12.23}$$

We are writing this in this particular way to make a point. Now also assume that

$$\langle \mathbf{r}|\psi\rangle = Y_{lm}(\theta,\phi) \tag{12.24}$$

so we find

$$\begin{aligned}\langle \mathbf{r}|\, U[M]\,|\psi\rangle &= \sum_{m''} Y_{lm''}(\theta,\phi)D^{(j)}_{m''m}\\ &= Y_{lm}(\theta,\phi)\end{aligned} \tag{12.25}$$

$$Y_{lm}(\theta,\phi) = Y_{lm}(x,y,z) \tag{12.26}$$

so

$$Y'_{lm}(x,y,z) = \sum_{m''} Y_{lm''}(x,y,z) D^{(j)}_{m''m} \tag{12.27}$$

Now consider the spherical harmonic as an operator $Y_{lm}(X,Y,Z)$

$$U[M] Y_{lm}(X,Y,Z) U^{\dagger}[M] = \sum_{m''} Y_{lm''}(X,Y,Z) D^{(j)}_{m''m} \tag{12.28}$$

So this is a way to generate spherical tensor operators of rank $0, 1, 2, \cdots$.

12.6 SPHERICAL TENSORS (CONT)

READING: §29 of [4].

definition . Any $(2k+1)$ operator $T(k,q)$, $q = -k, \cdots, k$ are the elements of a spherical tensor of rank k if

$$U[M] T(k,q) U^{-1}[M] = \sum_{q'} T(k,q') D^{(k)}_{qq'} \tag{12.29}$$

where $D^{(k)}_{qq'}$ was the matrix element of the rotation operator

$$D^{(k)}_{qq'} = \langle kq' | \, U[M] \, | kq'' \rangle \, . \tag{12.30}$$

So, if we have a Cartesian vector operator with components V_x, V_y, V_z then we can construct a corresponding spherical vector operator

$$\begin{aligned} T(1,1) &= -\tfrac{V_x + iV_y}{\sqrt{2}} \equiv V_{+1} \\ T(1,0) &= V_z \equiv V_0 \\ T(1,-1) &= -\tfrac{V_x - iV_y}{\sqrt{2}} \equiv V_{-1} \end{aligned} \quad . \tag{12.31}$$

By considering infinitesimal rotations we can come up with the commutation relations between the angular momentum operators

$$\begin{aligned}[J_\pm, T(k,q)] &= \hbar\sqrt{(k\mp q)(k\pm q+1)}T(k,q\pm 1)\\ [J_z, T(k,q)] &= \hbar q T(k,q)\end{aligned} \tag{12.32}$$

Note that the text in (29.15) defines these, whereas in class these were considered consequences of eq. (12.29), once infinitesimal rotations were used.

Recall that these match our angular momentum raising and lowering identities

$$\begin{aligned}J_\pm |kq\rangle &= \hbar\sqrt{(k\mp q)(k\pm q+1)}\,|k, q\pm 1\rangle\\ J_z |kq\rangle &= \hbar q\,|k,q\rangle\,.\end{aligned} \tag{12.33}$$

Consider two problems

$$\begin{array}{lcl} T(k,q) & & |kq\rangle \\ [J_\pm, T(k,q)] & \leftrightarrow & J_\pm |kq\rangle \\ [J_z, T(k,q)] & \leftrightarrow & J_z |kq\rangle \end{array} \tag{12.34}$$

We have a correspondence between the spherical tensors and angular momentum kets

$$\begin{array}{llll} T_1(k_1,q_1) & q_1 = -k_1,\cdots,k_1 & |k_1 q_1\rangle & |k_2 q_2\rangle \\ T_2(k_2,q_2) & q_2 = -k_2,\cdots,k_2 & q_1 = -k_1,\cdots k_1 & q_2 = -k_2,\cdots k_2 \end{array} \tag{12.35}$$

So, as we can write for angular momentum

These are the C.G coefficients

$$\begin{aligned}|kq\rangle &= \sum_{q_1,q_2} |k_1,q_1\rangle\,|k_2,q_2\rangle\,\boxed{\langle k_1 q_1 k_2 q_2 | kq\rangle}\\ |k_1 q_1; k_2 q_2\rangle &= \sum_{k,q'} \left|kq'\right\rangle \left\langle kq'\right| k_1 q_1 k_2 q_2\rangle\end{aligned} \tag{12.36}$$

We also have for spherical tensors

$$\begin{aligned}T(k,q) &= \sum_{q_1,q_2} T_1(k_1,q_1)T_2(k_2,q_2)\,\langle k_1 q_1 k_2 q_2 | kq\rangle\\ T_1(k_1,q_1)T_2(k_2,q_2) &= \sum_{k,q'} T(k,q')\,\langle kq'\left| k_1 q_1 k_2 q_2\right\rangle\end{aligned} \tag{12.37}$$

Can form eigenstates $|kq\rangle$ of (total angular momentum)^2 and (z-comp of the total angular momentum). FIXME: this will not be proven, but we are strongly suggested to try this ourselves.

$$\begin{array}{lcl} \text{spherical tensor (3)} & \leftrightarrow & \text{Cartesian vector (3)} \\ \text{(spherical vector)(spherical vector)} & & \text{Cartesian tensor} \end{array} \tag{12.38}$$

We can check the dimensions for a spherical tensor decomposition into rank 0, rank 1 and rank 2 tensors.

$$\begin{array}{lll} \text{spherical tensor rank 0} & (1) & \text{(Cartesian vector)(Cartesian vector)} \\ \text{spherical tensor rank 1} & (3) & (3)(3) \\ \text{spherical tensor rank 2} & (5) & 9 \\ \hline \text{dimension check sum} & 9 & \end{array} \tag{12.39}$$

Or in the direct product and sum shorthand

$$1 \otimes 1 = 0 \oplus 1 \oplus 2 \tag{12.40}$$

Note that this is just like problem 4 in problem set 10 where we calculated the CG kets for the $1 \otimes 1 = 0 \oplus 1 \oplus 2$ decomposition starting from kets $|1m\rangle\,|1m'\rangle$.

$$\begin{array}{ccccc} |22\rangle & & & & \\ |21\rangle & |11\rangle & & & \\ |20\rangle & |10\rangle & |00\rangle & & \\ \left|2\bar{1}\right\rangle & \left|1\bar{1}\right\rangle & & & \\ \left|2\bar{2}\right\rangle & & & & \end{array} \tag{12.41}$$

Example .

How about a Cartesian tensor of rank 3?

$$A_{ijk} \tag{12.42}$$

$$\begin{aligned} 1 \otimes 1 \otimes 1 &= 1 \otimes (0 \oplus 1 \oplus 2) \\ &= (1 \otimes 0) \oplus (1 \otimes 1) \oplus (1 \otimes 2) \\ &= \begin{array}{ccccccccccccc} 1 & \oplus & (0 & \oplus & 1 & \oplus & 2) & \oplus & (3 & \oplus & 2 & \oplus & 1) \\ 3 & + & 1 & + & 3 & + & 5 & + & 7 & + & 5 & + & 3 = 27 \end{array} \end{aligned} \tag{12.43}$$

Why bother? Consider a tensor operator $T(k,q)$ and an eigenket of angular momentum $|\alpha\, jm\rangle$, where α is a degeneracy index.

Look at

$$\begin{aligned} T(k,q)\,|\alpha\, jm\rangle\, U[M]T(k,q)\,|\alpha\, jm\rangle &= U[M]T(k,q)U^{\dagger}[M]U[M]\,|\alpha\, jm\rangle \\ &= \sum_{q'm'} D^{(k)}_{qq'} D^{(j)}_{mm'} T(k,q')\,\big|\alpha\, jm'\big\rangle \end{aligned} \tag{12.44}$$

This transforms like $|kq\rangle \otimes |jm\rangle$. We can say immediately

$$\big\langle \alpha' j' m' \big|\, T(k,q)\,|\alpha\, jm\rangle = 0 \tag{12.45}$$

unless

$$\begin{aligned} |k-j| \le j' &\le k+j \\ m' &= m+q \end{aligned} \tag{12.46}$$

This is the "selection rule".

Examples.

- Scalar $T(0,0)$

$$\big\langle \alpha' j' m' \big|\, T(0,0)\,|\alpha\, jm\rangle = 0, \tag{12.47}$$

unless $j = j'$ and $m = m'$.

- V_x, V_y, V_z. What are the non-vanishing matrix elements?

$$V_x = \frac{V_{-1} - V_{+1}}{\sqrt{2}}, \cdots \tag{12.48}$$

$$\big\langle \alpha' j' m' \big|\, V_{x,y}\,|\alpha\, jm\rangle = 0, \tag{12.49}$$

unless

$$\begin{aligned} |j-1| \le j' &\le j+1 \\ m' &= m \pm 1 \end{aligned} \tag{12.50}$$

$$\langle \alpha' j' m' \big| V_z \, | \alpha j m \rangle = 0, \tag{12.51}$$

unless

$$\begin{aligned} |j-1| \leq j' &\leq j+1 \\ m' &= m \end{aligned} \tag{12.52}$$

Very generally one can prove (the Wigner-Eckart theory in the text §29.3)

$$\langle \alpha_2 j_2 m_2 | \, T(k,q) \, | \alpha_1 j_1 m_1 \rangle = \langle \alpha_2 j_2 | \, T(k) \, | \alpha_1 j_1 \rangle \cdot \langle j_2 m_2 | k q_1 ; j_1 m_1 \rangle \tag{12.53}$$

where we split into a "reduced matrix element" describing the "physics", and the CG coefficient for "geometry" respectively.

Part III

SCATTERING THEORY

13

SCATTERING THEORY

13.1 SETUP

READING: §19, §20 of the text [4].

Figure 13.1 shows a simple classical picture of a two particle scattering collision

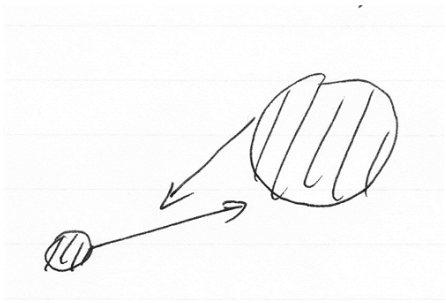

Figure 13.1: classical collision of particles

We will focus on point particle elastic collisions (no energy lost in the collision). With particles of mass m_1 and m_2 we write for the total and reduced mass respectively

$$M = m_1 + m_2 \tag{13.1}$$

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}, \tag{13.2}$$

so that interaction due to a potential $V(\mathbf{r}_1 - \mathbf{r}_2)$ that depends on the difference in position $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}$ has, in the center of mass frame, the Hamiltonian

$$H = \frac{\mathbf{p}^2}{2\mu} + V(\mathbf{r}) \tag{13.3}$$

In the classical picture we would investigate the scattering radius r_0 associated with the impact parameter ρ as depicted in fig. 13.2

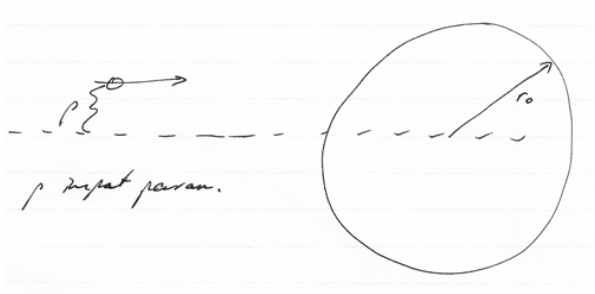

Figure 13.2: Classical scattering radius and impact parameter

13.2 1D QM SCATTERING. NO POTENTIAL WAVE PACKET TIME EVOLUTION

Now lets move to the QM picture where we assume that we have a particle that can be represented as a wave packet as in fig. 13.3

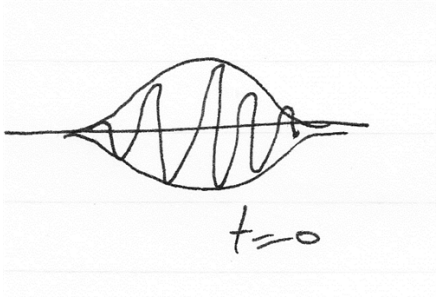

Figure 13.3: Wave packet for a particle wavefunction $\Re(\psi(x,0))$

First without any potential $V(x) = 0$, lets consider the evolution. Our position and momentum space representations are related by

$$\int |\psi(x,t)|^2 dx = 1 = \int |\psi(p,t)|^2 dp, \tag{13.4}$$

and by Fourier transform

$$\psi(x,t) = \int \frac{dp}{\sqrt{2\pi\hbar}} \overline{\psi}(p,t) e^{ipx/\hbar}. \tag{13.5}$$

Schrödinger's equation takes the form

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi(x,t)}{\partial x^2}, \tag{13.6}$$

or more simply in momentum space

$$i\hbar\frac{\partial\overline{\psi}(p,t)}{\partial t} = \frac{p^2}{2\mu}\frac{\partial^2\overline{\psi}(p,t)}{\partial x^2}. \tag{13.7}$$

Rearranging to integrate we have

$$\frac{\partial\overline{\psi}}{\partial t} = -\frac{ip^2}{2\mu\hbar}\overline{\psi}, \tag{13.8}$$

and integrating

$$\ln\overline{\psi} = -\frac{ip^2t}{2\mu\hbar} + \ln C, \tag{13.9}$$

or

$$\overline{\psi} = Ce^{-\frac{ip^2t}{2\mu\hbar}} = \overline{\psi}(p,0)e^{-\frac{ip^2t}{2\mu\hbar}}. \tag{13.10}$$

Time evolution in momentum space for the free particle changes only the phase of the wavefunction, the momentum probability density of that particle.

Fourier transforming, we find our position space wavefunction to be

$$\psi(x,t) = \int\frac{dp}{\sqrt{2\pi\hbar}}\overline{\psi}(p,0)e^{ipx/\hbar}e^{-ip^2t/2\mu\hbar}. \tag{13.11}$$

To clean things up, write

$$p = \hbar k, \tag{13.12}$$

for

$$\psi(x,t) = \int\frac{dk}{\sqrt{2\pi}}a(k,0))e^{ikx}e^{-i\hbar k^2t/2\mu}, \tag{13.13}$$

where

$$a(k,0) = \sqrt{\hbar}\overline{\psi}(p,0). \tag{13.14}$$

Putting

$$a(k,t) = a(k,0)e^{-i\hbar k^2/2\mu}, \tag{13.15}$$

we have

$$\psi(x,t) = \int \frac{dk}{\sqrt{2\pi}} a(k,t))e^{ikx} \tag{13.16}$$

Observe that we have

$$\int dk|a(k,t)|^2 = \int dp\left|\overline{\psi}(p,t)\right|^2 = 1. \tag{13.17}$$

13.3 A GAUSSIAN WAVE PACKET

Suppose that we have, as depicted in fig. 13.4

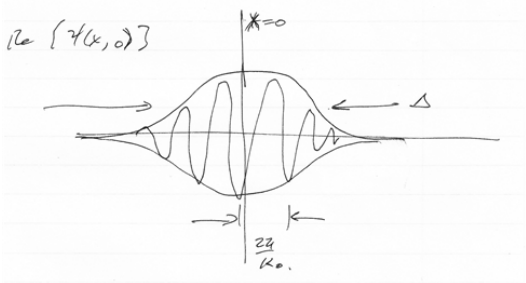

Figure 13.4: Gaussian wave packet

a Gaussian wave packet of the form

$$\psi(x,0) = \frac{(\pi\Delta^2)^{1/4}}{e}\, e^{ik_0 x} e^{-x^2/2\Delta^2}. \tag{13.18}$$

This is actually a minimum uncertainty packet with

$$\begin{aligned} \Delta x &= \frac{\Delta}{\sqrt{2}} \\ \Delta p &= \frac{\hbar}{\Delta\sqrt{2}}. \end{aligned} \tag{13.19}$$

Taking Fourier transforms we have

$$
\begin{aligned}
a(k,0) &= \left(\frac{\Delta^2}{\pi}\right)^{1/4} e^{-(k-k_0)^2\Delta^2/2} \\
a(k,t) &= \left(\frac{\Delta^2}{\pi}\right)^{1/4} e^{-(k-k_0)^2\Delta^2/2} e^{-i\hbar k^2 t/2\mu} \equiv \alpha(k,t)
\end{aligned}
\tag{13.20}
$$

For $t > 0$ our wave packet will start moving and spreading as in fig. 13.5

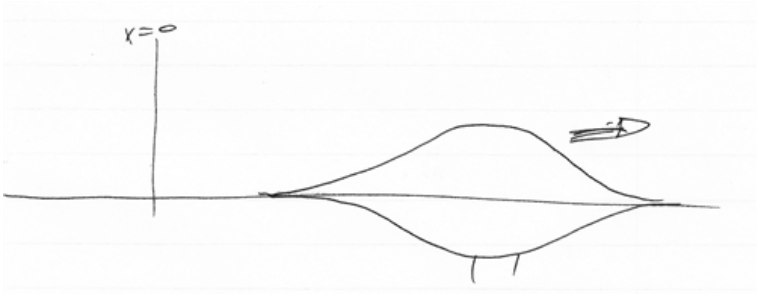

Figure 13.5: moving spreading Gaussian packet

13.4 WITH A POTENTIAL

Now "switch on" a potential, still assuming a wave packet representation for the particle. With a positive (repulsive) potential as in fig. 13.6, at a time long before the interaction of the wave packet with the potential we can visualize the packet as heading towards the barrier.

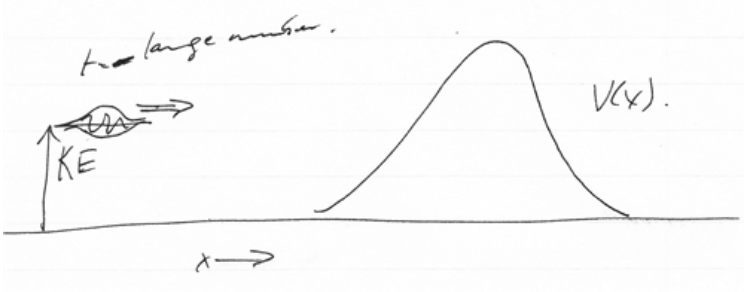

Figure 13.6: QM wave packet prior to interaction with repulsive potential

After some time long after the interaction, classically for this sort of potential where the particle kinetic energy is less than the barrier "height", we would have total reflection. In the

QM case, we have seen before that we will have a reflected and a transmitted portion of the wave packet as depicted in fig. 13.7

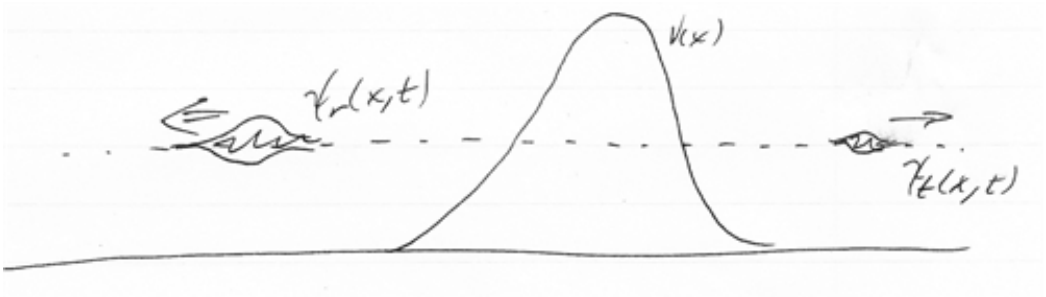

Figure 13.7: QM wave packet long after interaction with repulsive potential

Even if the particle kinetic energy is greater than the barrier height, as in fig. 13.8, we can still have a reflected component.

Figure 13.8: Kinetic energy greater than potential energy

This is even true for a negative potential as depicted in fig. 13.9!

Consider the probability for the particle to be found anywhere long after the interaction, summing over the transmitted and reflected wave functions, we have

$$\begin{aligned} 1 &= \int |\psi_r + \psi_t|^2 \\ &= \int |\psi_r|^2 + \int |\psi_t|^2 + 2\Re \int \psi_r^* \psi_t \end{aligned} \tag{13.21}$$

Observe that long after the interaction the cross terms in the probabilities will vanish because they are non-overlapping, leaving just the probably densities for the transmitted and reflected probably densities independently.

Figure 13.9: qmTwoL21Fig9

We define

$$\begin{aligned} T &= \int |\psi_t(x,t)|^2 dx \\ R &= \int |\psi_r(x,t)|^2 dx. \end{aligned} \tag{13.22}$$

The objective of most of our scattering problems will be the calculation of these probabilities and the comparisons of their ratios.

Question . Can we have more than one wave packet reflect off. Yes, we could have multiple wave packets for both the reflected and the transmitted portions. For example, if the potential has some internal structure there could be internal reflections before anything emerges on either side and things could get quite messy.

13.5 CONSIDERING THE TIME INDEPENDENT CASE TEMPORARILY

We are going to work through something that is going to seem at first to be completely unrelated. We will (eventually) see that this can be applied to this problem, so a bit of patience will be required.

We will be using the time independent Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\psi_k''(x) = V(x)\psi_k(x) = E\psi_k(x), \tag{13.23}$$

where we have added a subscript k to our wave function with the intention (later) of allowing this to vary. For "future use" we define for $k > 0$

$$E = \frac{\hbar^2 k^2}{2\mu}. \tag{13.24}$$

Consider a potential as in fig. 13.10, where $V(x) = 0$ for $x > x_2$ and $x < x_1$.

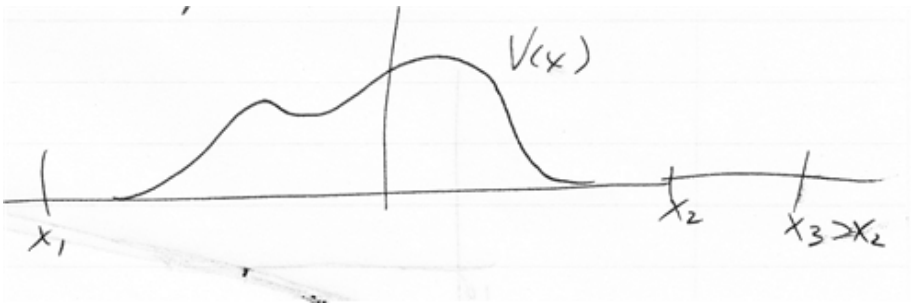

Figure 13.10: potential zero outside of a specific region

We will not have bound states here (repulsive potential). There will be many possible solutions, but we want to look for a solution that is of the form

$$\psi_k(x) = Ce^{ikx}, \qquad x > x_2 \tag{13.25}$$

Suppose $x = x_3 > x_2$, we have

$$\psi_k(x_3) = Ce^{ikx_3} \tag{13.26}$$

$$\left.\frac{d\psi_k}{dx}\right|_{x=x_3} = ikCe^{ikx_3} \equiv \phi_k(x_3) \tag{13.27}$$

$$\left.\frac{d^2\psi_k}{dx^2}\right|_{x=x_3} = -k^2 Ce^{ikx_3} \tag{13.28}$$

Defining

$$\phi_k(x) = \frac{d\psi_k}{dx}, \tag{13.29}$$

we write Schrödinger's equation as a pair of coupled first order equations

$$\begin{aligned} \frac{d\psi_k}{dx} &= \phi_k(x) \\ -\frac{\hbar^2}{2\mu}\frac{d\phi_k(x)}{dx} &= -V(x)\psi_k(x) + \frac{\hbar^2 k^2}{2\mu}\psi_k(x). \end{aligned} \tag{13.30}$$

At this $x = x_3$ specifically, we "know" both $\phi_k(x_3)$ and $\psi_k(x_3)$ and have

$$\begin{aligned} \left.\frac{d\psi_k}{dx}\right|_{x_3} &= \phi_k(x) \\ -\frac{\hbar^2}{2\mu}\left.\frac{d\phi_k(x)}{dx}\right|_{x_3} &= -V(x_3)\psi_k(x_3) + \frac{\hbar^2 k^2}{2\mu}\psi_k(x_3), \end{aligned} \tag{13.31}$$

This allows us to find both

$$\begin{aligned} &\left.\frac{d\psi_k}{dx}\right|_{x_3} \\ &\left.\frac{d\phi_k(x)}{dx}\right|_{x_3} \end{aligned} \tag{13.32}$$

then proceed to numerically calculate $\phi_k(x)$ and $\psi_k(x)$ at neighboring points $x = x_3 + \epsilon$. Essentially, this allows us to numerically integrate backwards from x_3 to find the wave function at previous points for any sort of potential.

13.6 RECAP

READING: §19, §20 of the text [4].

We used a positive potential of the form of fig. 13.11

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2\psi_k(x)}{\partial x^2} + V(x)\psi_k(x) = \frac{\hbar^2 k^2}{2\mu} \tag{13.33}$$

for $x \geq x_3$

$$\psi_k(x) = Ce^{ikx} \tag{13.34}$$

$$\phi_k(x) = \frac{d\psi_k(x)}{dx} \tag{13.35}$$

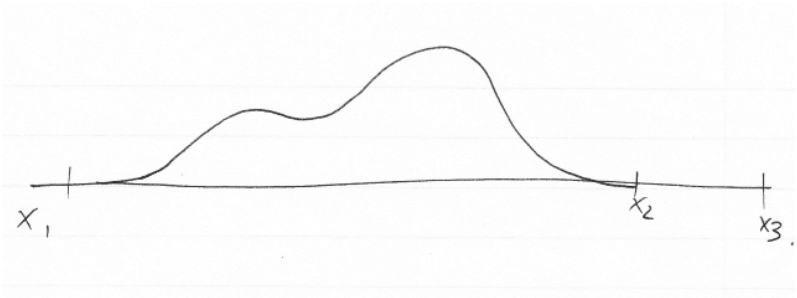

Figure 13.11: A bounded positive potential

for $x \geq x_3$

$$\phi_k(x) = ikCe^{ikx} \tag{13.36}$$

$$\begin{aligned} \frac{d\psi_k(x)}{dx} &= \phi_k(x) \\ -\frac{\hbar^2}{2\mu}\frac{d\phi_k(x)}{dx} &= -V(x)\psi_k(x) + \frac{\hbar^2 k^2}{2\mu} \end{aligned} \tag{13.37}$$

integrate these equations back to x_1.
For $x \leq x_1$

$$\psi_k(x) = Ae^{ikx} + Be^{-ikx}, \tag{13.38}$$

where both A and B are proportional to C, dependent on k.
There are cases where we can solve this analytically (one of these is on our problem set).
Alternatively, write as (so long as $A \neq 0$)

$$\begin{aligned} \psi_k(x) &\to e^{ikx} + \beta_k e^{-ikx} \qquad \text{for } x < x_1 \\ &\to \gamma_k e^{ikx} \qquad\qquad\quad \text{for } x > x_2 \end{aligned} \tag{13.39}$$

Now want to consider the problem of no potential in the interval of interest, and our window bounded potential as in fig. 13.12

where we model our particle as a wave packet as we found can have the fourier transform description, for $t_{\text{initial}} < 0$, of

$$\psi(x, t_{\text{initial}}) = \int \frac{dk}{\sqrt{2\pi}} \alpha(k, t_{\text{initial}}) e^{ikx} \tag{13.40}$$

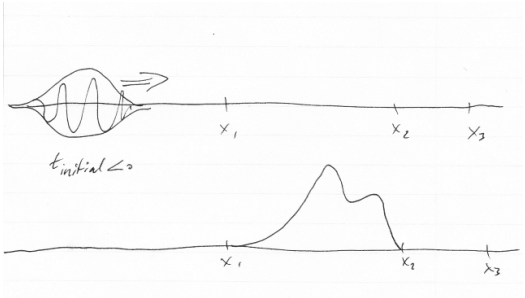

Figure 13.12: Wave packet in free space and with positive potential

Returning to the same coefficients, the solution of the Schrödinger eqn for problem with the potential eq. (13.39)

For $x \leq x_1$,

$$\psi(x,t) = \psi_i(x,t) + \psi_r(x,t) \tag{13.41}$$

where as illustrated in fig. 13.13

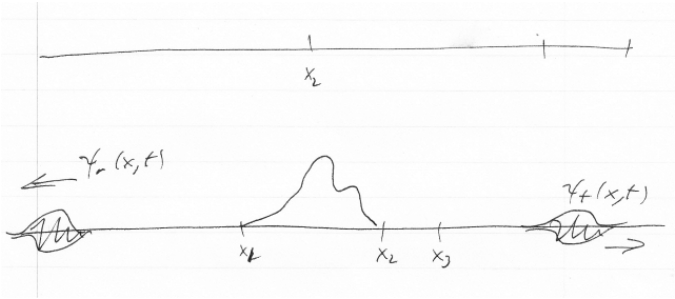

Figure 13.13: Reflection and transmission of wave packet

$$\begin{aligned} \psi_i(x,t) &= \int \frac{dk}{\sqrt{2\pi}} \alpha(k, t_{\text{initial}}) e^{ikx} \\ \psi_r(x,t) &= \int \frac{dk}{\sqrt{2\pi}} \alpha(k, t_{\text{initial}}) \beta_k e^{-ikx}. \end{aligned} \tag{13.42}$$

For $x > x_2$

$$\psi(x,t) = \psi_t(x,t) \tag{13.43}$$

and

$$\psi_t(x,t) = \int \frac{dk}{\sqrt{2\pi}} \alpha(k, t_{\text{initial}}) \gamma_k e^{ikx} \tag{13.44}$$

Look at

$$\psi_r(x,t) = \chi(-x,t) \tag{13.45}$$

where

$$\begin{aligned} \chi(x,t) &= \int \frac{dk}{\sqrt{2\pi}} \alpha(k, t_{\text{initial}}) \beta_k e^{ikx} \\ &\approx \beta_{k_0} \int \frac{dk}{\sqrt{2\pi}} \alpha(k, t_{\text{initial}}) e^{ikx} \end{aligned} \tag{13.46}$$

for $t = t_{\text{initial}}$, this is nonzero for $x < x_1$.
so for $x < x_1$

$$\psi_r(x, t_{\text{initial}}) = 0 \tag{13.47}$$

In the same way, for $x > x_2$

$$\psi_t(x, t_{\text{initial}}) = 0. \tag{13.48}$$

What has not been proved is that the wavefunction is also zero in the $[x_1, x_2]$ interval.

Summarizing For $t = t_{\text{initial}}$

$$\psi(x, t_{\text{initial}}) = \begin{cases} \int \frac{dk}{\sqrt{2\pi}} \alpha(k, t_{\text{initial}}) e^{ikx} & \text{for } x < x_1 \\ 0 & \text{for } x > x_2 \text{ (and actually also for } x > x_1 \text{ (unproven))} \end{cases} \tag{13.49}$$

for $t = t_{\text{final}}$

$$\psi(x, t_{\text{final}}) \to \begin{cases} \int \frac{dk}{\sqrt{2\pi}} \beta_k \alpha(k, t_{\text{final}}) e^{-ikx} & \text{for } x < x_1 \\ 0 & x \in [x_1, x_2] \\ \int \frac{dk}{\sqrt{2\pi}} \gamma_k \alpha(k, t_{\text{final}}) e^{ikx} & \text{for } x > x_2 \end{cases} \tag{13.50}$$

Probability of reflection is

$$\int |\psi_r(x, t_{\text{final}})|^2 dx \tag{13.51}$$

If we have a sufficiently localized packet, we can form a first order approximation around the peak of β_k (FIXME: or is this a sufficiently localized responce to the potential on reflection?)

$$\psi_r(x, t_{\text{final}}) \approx \beta_{k_0} \int \frac{dk}{\sqrt{2\pi}} \alpha(k, t_{\text{final}}) e^{-ikx}, \tag{13.52}$$

so

$$\int |\psi_r(x, t_{\text{final}})|^2 dx \approx \left|\beta_{k_0}\right|^2 \equiv R \tag{13.53}$$

Probability of transmission is

$$\int |\psi_t(x, t_{\text{final}})|^2 dx \tag{13.54}$$

Again, assuming a small spread in γ_k, with $\gamma_k \approx \gamma_{k_0}$ for some k_0

$$\psi_t(x, t_{\text{final}}) \approx \gamma_{k_0} \int \frac{dk}{\sqrt{2\pi}} \alpha(k, t_{\text{final}}) e^{ikx}, \tag{13.55}$$

we have for $x > x_2$

$$\int |\psi_t(x, t_{\text{final}})|^2 dx \approx \left|\gamma_{k_0}\right|^2 \equiv T. \tag{13.56}$$

By constructing the wave packets in this fashion we get as a side effect the solution of the scattering problem.

The

$$\begin{aligned} \psi_k(x) \to & e^{ikx} + \beta_k e^{-ikx} \\ & \gamma_k e^{ikx} \end{aligned} \tag{13.57}$$

are called asymptotic in states. Their physical applicability is only once we have built wave packets out of them.

14

3D SCATTERING

14.1 SETUP

READING: §20, and §4.8 of our text [4].

For a potential $V(\mathbf{r}) \approx 0$ for $r > r_0$ as in fig. 14.1

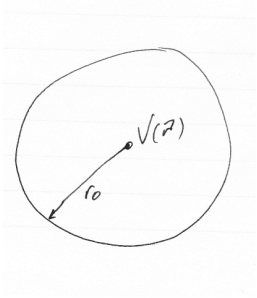

Figure 14.1: Radially bounded spherical potential

From 1D we have learned to build up solutions from time independent solutions (non normalizable). Consider an incident wave

$$e^{i\mathbf{k}\cdot\mathbf{r}} = e^{ik\hat{\mathbf{n}}\cdot\mathbf{r}} \tag{14.1}$$

This is a solution of the time independent Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\boldsymbol{\nabla}^2 e^{i\mathbf{k}\cdot\mathbf{r}} = E e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{14.2}$$

where

$$E = \frac{\hbar^2\mathbf{k}^2}{2\mu}. \tag{14.3}$$

In the presence of a potential expect scattered waves.

Consider scattering off of a positive potential as depicted in fig. 14.2

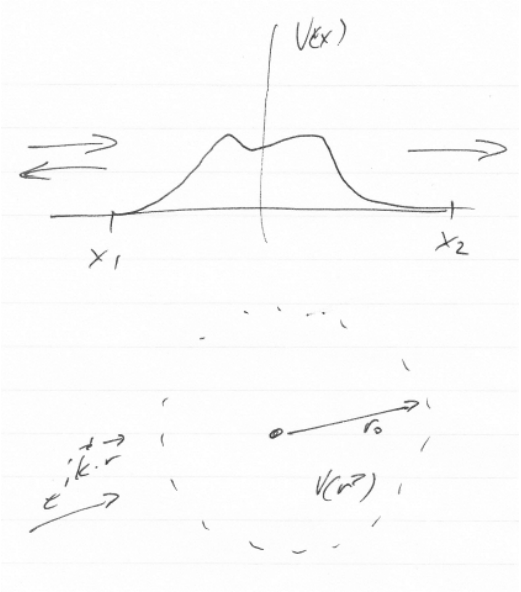

Figure 14.2: Radially bounded potential

Here we have $V(r) = 0$ for $r > r_0$. The wave function

$$e^{ik\hat{\mathbf{n}}\cdot\mathbf{r}} \tag{14.4}$$

is found to be a solution of the free particle Schrödinger equation.

$$-\frac{\hbar^2}{2\mu}\boldsymbol{\nabla}^2 e^{ik\hat{\mathbf{n}}\cdot\mathbf{r}} = \frac{\hbar^2\mathbf{k}^2}{2\mu}e^{ik\hat{\mathbf{n}}\cdot\mathbf{r}} \tag{14.5}$$

14.2 SEEKING A POST SCATTERING SOLUTION AWAY FROM THE POTENTIAL

What other solutions can be found for $r > r_0$, where our potential $V(r) = 0$? We are looking for $\Phi(\mathbf{r})$ such that

$$-\frac{\hbar^2}{2\mu}\boldsymbol{\nabla}^2\Phi(r) = \frac{\hbar^2\mathbf{k}^2}{2\mu}\Phi(r) \tag{14.6}$$

What can we find?

We split our Laplacian into radial and angular components as we did for the hydrogen atom

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}(r\Phi(\mathbf{r})) + \frac{\mathcal{L}^2}{2\mu r^2}\Phi(\mathbf{r}) = E\Phi(\mathbf{r}), \tag{14.7}$$

where

$$\mathcal{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial+}{\partial\theta}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) \tag{14.8}$$

Assuming a solution of

$$\Phi(\mathbf{r}) = R(r)Y_l^m(\theta,\phi), \tag{14.9}$$

and noting that

$$\mathcal{L}^2 Y_l^m(\theta,\phi) = \hbar^2 l(l+1)Y_l^m(\theta,\phi), \tag{14.10}$$

we find that our radial equation becomes

$$-\frac{\hbar^2}{2\mu r}\frac{\partial^2}{\partial r^2}(rR(r)) + \frac{\hbar^2 l(l+1)}{2\mu r^2}R(r) = ER(r) = \frac{\hbar^2 k^2}{2\mu}R(r). \tag{14.11}$$

Writing

$$R(r) = \frac{u(r)}{r}, \tag{14.12}$$

we have

$$-\frac{\hbar^2}{2\mu r}\frac{\partial^2 u(r)}{\partial r^2} + \frac{\hbar^2 l(l+1)}{2\mu r}u(r) = \frac{\hbar^2 k^2}{2\mu}\frac{u(r)}{r}, \tag{14.13}$$

or

$$\left(\frac{d^2}{dr^2} + k^2 - \frac{l(l+1)}{r^2}\right)u(r) = 0 \tag{14.14}$$

Writing $\rho = kr$, we have

$$\left(\frac{d^2}{d\rho^2} + 1 - \frac{l(l+1)}{\rho^2}\right)u(r) = 0 \tag{14.15}$$

14.3 THE RADIAL EQUATION AND ITS SOLUTION

With a last substitution of $u(r) = U(kr) = U(\rho)$, and introducing an explicit l suffix on our eigenfunction $U(\rho)$ we have

$$\left(-\frac{d^2}{d\rho^2} + \frac{l(l+1)}{\rho^2}\right) U_l(\rho) = U_l(\rho). \tag{14.16}$$

We would not have done this before with the hydrogen atom since we had only finite $E = \hbar^2 k^2/2\mu$. Now this can be anything.

Making one final substitution, $U_l(\rho) = \rho f_l(\rho)$ we can rewrite eq. (14.16) as

$$\left(\rho^2 \frac{d^2}{d\rho^2} + 2\rho\frac{d}{d\rho} + (\rho^2 - l(l+1))\right) f_l = 0. \tag{14.17}$$

This is the spherical Bessel equation of order l and has solutions called the Bessel and Neumann functions of order l, which are

$$j_l(\rho) = (-\rho)^l \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l \left(\frac{\sin\rho}{\rho}\right) \tag{14.18a}$$

$$n_l(\rho) = (-\rho)^l \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l \left(-\frac{\cos\rho}{\rho}\right). \tag{14.18b}$$

We can easily calculate

$$\begin{aligned} U_0(\rho) &= \rho j_0(\rho) = \sin\rho \\ U_1(\rho) &= \rho j_1(\rho) = -\cos\rho + \frac{\sin\rho}{\rho} \end{aligned} \tag{14.19}$$

and can plug these into eq. (14.16) to verify that they are a solution. A more general proof looks a bit trickier.

Observe that the Neumann functions are less well behaved at the origin. To calculate the first few Bessel and Neumann functions we first compute

$$\begin{aligned} \frac{1}{\rho}\frac{d}{d\rho}\frac{\sin\rho}{\rho} &= \frac{1}{\rho}\left(\frac{\cos\rho}{\rho} - \frac{\sin\rho}{\rho^2}\right) \\ &= \frac{\cos\rho}{\rho^2} - \frac{\sin\rho}{\rho^3} \end{aligned} \tag{14.20}$$

$$\begin{aligned}\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^2\frac{\sin\rho}{\rho} &= \frac{1}{\rho}\left(-\frac{\sin\rho}{\rho^2}-2\frac{\cos\rho}{\rho^3}-\frac{\cos\rho}{\rho^3}+3\frac{\sin\rho}{\rho^4}\right)\\ &= \sin\rho\left(-\frac{1}{\rho^3}+\frac{3}{\rho^5}\right)-3\frac{\cos\rho}{\rho^4}\end{aligned} \tag{14.21}$$

and

$$\begin{aligned}\frac{1}{\rho}\frac{d}{d\rho}-\frac{\cos\rho}{\rho} &= \frac{1}{\rho}\left(\frac{\sin\rho}{\rho}+\frac{\cos\rho}{\rho^2}\right)\\ &= \frac{\sin\rho}{\rho^2}+\frac{\cos\rho}{\rho^3}\end{aligned} \tag{14.22}$$

$$\begin{aligned}\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^2-\frac{\cos\rho}{\rho} &= \frac{1}{\rho}\left(\frac{\cos\rho}{\rho^2}-2\frac{\sin\rho}{\rho^3}-\frac{\sin\rho}{\rho^3}-3\frac{\cos\rho}{\rho^4}\right)\\ &= \cos\rho\left(\frac{1}{\rho^3}-\frac{3}{\rho^5}\right)-3\frac{\sin\rho}{\rho^4}\end{aligned} \tag{14.23}$$

so we find

$$\begin{aligned} j_0(\rho) &= \tfrac{\sin\rho}{\rho} & n_0(\rho) &= -\tfrac{\cos\rho}{\rho}\\ j_1(\rho) &= \tfrac{\sin\rho}{\rho^2}-\tfrac{\cos\rho}{\rho} & n_1(\rho) &= -\tfrac{\cos\rho}{\rho^2}-\tfrac{\sin\rho}{\rho}\\ j_2(\rho) &= \sin\rho\left(-\tfrac{1}{\rho}+\tfrac{3}{\rho^3}\right)+\cos\rho\left(-\tfrac{3}{\rho^2}\right) & n_2(\rho) &= \cos\rho\left(\tfrac{1}{\rho}-\tfrac{3}{\rho^3}\right)+\sin\rho\left(-\tfrac{3}{\rho^2}\right)\end{aligned} \tag{14.24}$$

Observe that our radial functions $R(r)$ are proportional to these Bessel and Neumann functions

$$\begin{aligned} R(r) &= \frac{u(r)}{r}\\ &= \frac{U(kr)}{r}\\ &= \begin{cases} \frac{j_l(\rho)\rho}{r}\\ \frac{n_l(\rho)\rho}{r}\end{cases}\\ &= \begin{cases} \frac{j_l(\rho)k\not{r}}{\not{r}}\\ \frac{n_l(\rho)k\not{r}}{\not{r}}\end{cases}\end{aligned} \tag{14.25}$$

Or

$$R(r) \sim j_l(\rho), n_l(\rho). \tag{14.26}$$

14.4 LIMITS OF SPHERICAL BESSEL AND NEUMANN FUNCTIONS

With $n!!$ denoting the double factorial, like factorial but skipping every other term

$$n!! = n(n-2)(n-4)\cdots, \tag{14.27}$$

we can show that in the limit as $\rho \to 0$ we have

$$j_l(\rho) \to \frac{\rho^l}{(2l+1)!!} \tag{14.28a}$$

$$n_l(\rho) \to -\frac{(2l-1)!!}{\rho^{(l+1)}}, \tag{14.28b}$$

(for the $l = 0$ case, note that $(-1)!! = 1$ by definition).

Comparing this to our explicit expansion for $j_1(\rho)$ in eq. (14.24) where we appear to have a $1/\rho$ dependence for small ρ it is not obvious that this would be the case. To compute this we need to start with a power series expansion for $\sin\rho/\rho$, which is well behaved at $\rho = 0$ and then the result follows (done later).

It is apparently also possible to show that as $\rho \to \infty$ we have

$$j_l(\rho) \to \frac{1}{\rho}\sin\left(\rho - \frac{l\pi}{2}\right) \tag{14.29a}$$

$$n_l(\rho) \to -\frac{1}{\rho}\cos\left(\rho - \frac{l\pi}{2}\right). \tag{14.29b}$$

14.5 BACK TO OUR PROBLEM

For $r > r_0$ we can construct (for fixed k) a superposition of the spherical functions

$$\sum_l \sum_m \left(A_l j_l(kr) + B_l n_l(kr)\right) Y_l^m(\theta, \phi) \tag{14.30}$$

we want outgoing waves, and as $r \to \infty$, we have

$$j_l(kr) \to \frac{\sin\left(kr - \frac{l\pi}{2}\right)}{kr} \tag{14.31a}$$

$$n_l(kr) \to -\frac{\cos\left(kr - \frac{l\pi}{2}\right)}{kr} \tag{14.31b}$$

Put $A_l/B_l = -i$ for a given l we have

$$\frac{1}{kr}\left(-i\frac{\sin\left(kr - \frac{l\pi}{2}\right)}{kr} - \frac{\cos\left(kr - \frac{l\pi}{2}\right)}{kr}\right) \sim \frac{1}{kr}e^{i(kr-\pi l/2)} \tag{14.32}$$

For

$$\sum_l \sum_m B_l \frac{1}{kr} e^{i(kr-\pi l/2)} Y_l^m(\theta, \phi). \tag{14.33}$$

Making this choice to achieve outgoing waves (and factoring a $(-i)^l$ out of B_l for some reason, we have another wave function that satisfies our Hamiltonian equation

$$\frac{e^{ikr}}{kr} \sum_l \sum_m (-1)^l B_l Y_l^m(\theta, \phi). \tag{14.34}$$

The B_l coefficients will depend on $V(r)$ for the incident wave $e^{i\mathbf{k}\cdot\mathbf{r}}$. Suppose we encapsulate that dependence in a helper function $f_{\mathbf{k}}(\theta, \phi)$ and write

$$\frac{e^{ikr}}{r} f_{\mathbf{k}}(\theta, \phi) \tag{14.35}$$

We seek a solution $\psi_{\mathbf{k}}(\mathbf{r})$

$$\left(-\frac{\hbar^2}{2\mu}\boldsymbol{\nabla}^2 + V(\mathbf{r})\right)\psi_{\mathbf{k}}(\mathbf{r}) = \frac{\hbar^2\mathbf{k}^2}{2\mu}\psi_{\mathbf{k}}(\mathbf{r}), \tag{14.36}$$

where as $r \to \infty$

$$\psi_{\mathbf{k}}(\mathbf{r}) \to e^{i\mathbf{k}\cdot\mathbf{r}} + \frac{e^{ikr}}{r} f_{\mathbf{k}}(\theta, \phi). \tag{14.37}$$

Note that for $r < r_0$ in general for finite r, $\psi_k(\mathbf{r})$, is much more complicated. This is the analogue of the plane wave result

$$\psi(x) = e^{ikx} + \beta_k e^{-ikx} \tag{14.38}$$

14.6 SCATTERING GEOMETRY AND NOMENCLATURE

We can think classically first, and imagine a scattering of a stream of particles barraging a target as in fig. 14.3

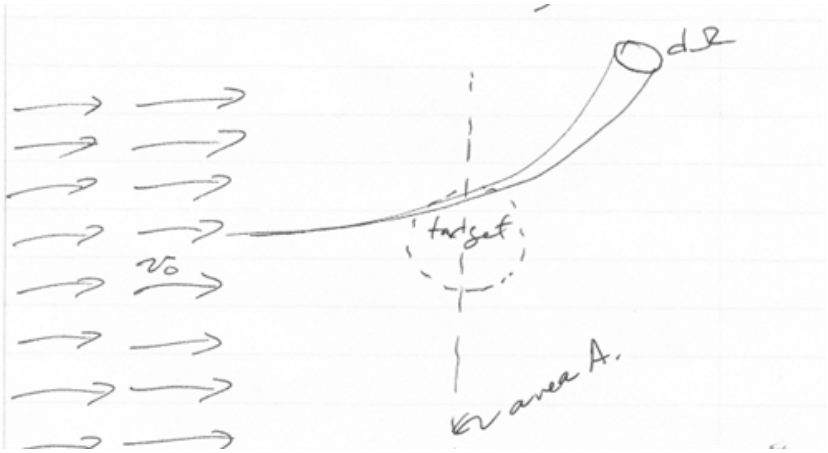

Figure 14.3: Scattering cross section

Here we assume that $d\Omega$ is far enough away that it includes no non-scattering particles. Write P for the number density

$$P = \frac{\text{number of particles}}{\text{unit volume}}, \tag{14.39}$$

and

$$J = Pv_0 = \frac{\text{Number of particles flowing through}}{\text{a unit area in unit time}} \tag{14.40}$$

We want to count the rate of particles per unit time dN through this solid angle $d\Omega$ and write

$$dN = J\left(\frac{d\sigma(\Omega)}{d\Omega}\right)d\Omega. \tag{14.41}$$

The factor

$$\frac{d\sigma(\Omega)}{d\Omega}, \tag{14.42}$$

is called the differential cross section, and has "units" of

$$\frac{\text{area}}{\text{steradians}} \tag{14.43}$$

(recalling that steradians are radian like measures of solid angle [18]).
The total number of particles through the volume per unit time is then

$$\int J \frac{d\sigma(\Omega)}{d\Omega} d\Omega = J \int \frac{d\sigma(\Omega)}{d\Omega} d\Omega = J\sigma \tag{14.44}$$

where σ is the total cross section and has units of area. The cross section σ his the effective size of the area required to collect all particles, and characterizes the scattering, but is not necessarily entirely geometrical. For example, in photon scattering we may have frequency matching with atomic resonance, finding $\sigma \sim \lambda^2$, something that can be much bigger than the actual total area involved.

14.7 APPENDIX

Q: Are Bessel and Neumann functions orthogonal?

Answer: There is an orthogonality relation, but it is not one of plain old multiplication.
Curious about this, I find an orthogonality condition in [16]

$$\int_0^\infty J_\alpha(z) J_\beta(z) \frac{dz}{z} = \frac{2}{\pi} \frac{\sin\left(\frac{\pi}{2}(\alpha - \beta)\right)}{\alpha^2 - \beta^2}, \tag{14.45}$$

from which we find for the spherical Bessel functions

$$\int_0^\infty j_l(\rho) j_m(\rho) d\rho = \frac{\sin\left(\frac{\pi}{2}(l - m)\right)}{(l + 1/2)^2 - (m + 1/2)^2}. \tag{14.46}$$

Is this a satisfactory orthogonality integral? At a glance it does not appear to be well behaved for $l = m$, but perhaps the limit can be taken?

Deriving the large limit Bessel and Neumann function approximations For eq. (14.29) we are referred to any "good book on electromagnetism" for details. I thought that perhaps the weighty

[8] would be to be such a book, but it also leaves out the details. In §16.1 the spherical Bessel and Neumann functions are related to the plain old Bessel functions with

$$j_l(x) = \sqrt{\frac{\pi}{2x}} J_{l+1/2}(x) \tag{14.47a}$$

$$n_l(x) = \sqrt{\frac{\pi}{2x}} N_{l+1/2}(x) \tag{14.47b}$$

Referring back to §3.7 of that text where the limiting forms of the Bessel functions are given

$$J_\nu(x) \to \sqrt{\frac{2}{\pi x}} \cos\left(x - \frac{\nu\pi}{2} - \frac{\pi}{4}\right) \tag{14.48a}$$

$$N_\nu(x) \to \sqrt{\frac{2}{\pi x}} \sin\left(x - \frac{\nu\pi}{2} - \frac{\pi}{4}\right) \tag{14.48b}$$

This does give us our desired identities, but there is no hint in the text how one would derive eq. (14.48) from the power series that was computed by solving the Bessel equation.

Deriving the small limit Bessel and Neumann function approximations Writing the sinc function in series form

$$\frac{\sin x}{x} = \sum_{k=0}^{\infty} (-1)^k \frac{x^{2k}}{(2k+1)!}, \tag{14.49}$$

we can differentiate easily

$$\begin{aligned} \frac{1}{x}\frac{d}{dx}\frac{\sin x}{x} &= \sum_{k=1}^{\infty} (-1)^k (2k) \frac{x^{2k-2}}{(2k+1)!} \\ &= (-1) \sum_{k=0}^{\infty} (-1)^k (2k+2) \frac{x^{2k}}{(2k+3)!} \\ &= (-1) \sum_{k=0}^{\infty} (-1)^k \frac{1}{2k+3} \frac{x^{2k}}{(2k+1)!} \end{aligned} \tag{14.50}$$

Performing the derivative operation a second time we find

$$\begin{aligned}\left(\frac{1}{x}\frac{d}{dx}\right)^2 \frac{\sin x}{x} &= (-1)\sum_{k=1}^{\infty}(-1)^k \frac{1}{2k+3}(2k)\frac{x^{2k-2}}{(2k+1)!} \\ &= \sum_{k=0}^{\infty}(-1)^k \frac{1}{2k+5}\frac{1}{2k+3}\frac{x^{2k}}{(2k+1)!}\end{aligned} \tag{14.51}$$

It appears reasonable to form the inductive hypotheses

$$\left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\sin x}{x} = (-1)^l \sum_{k=0}^{\infty}(-1)^k \frac{(2k+1)!\,!}{(2(k+l)+1)!\,!}\frac{x^{2k}}{(2k+1)!}, \tag{14.52}$$

and this proves to be correct. We find then that the spherical Bessel function has the power series expansion of

$$j_l(x) = \sum_{k=0}^{\infty}(-1)^k \frac{(2k+1)!\,!}{(2(k+l)+1)!\,!}\frac{x^{2k+l}}{(2k+1)!} \tag{14.53}$$

and from this the Bessel function limit of eq. (14.28a) follows immediately.

Finding the matching induction series for the Neumann functions is a bit harder. It is not really any more difficult to write it, but it is harder to put it in a tidy form that is.

We find

$$\begin{aligned}-\frac{\cos x}{x} &= -\sum_{k=0}^{\infty}(-1)^k \frac{x^{2k-1}}{(2k)!} \\ \frac{1}{x}\frac{d}{dx}-\frac{\cos x}{x} &= -\sum_{k=0}^{\infty}(-1)^k \frac{2k-1}{2k}\frac{x^{2k-3}}{(2k-2)!} \\ \left(\frac{1}{x}\frac{d}{dx}\right)^2-\frac{\cos x}{x} &= -\sum_{k=0}^{\infty}(-1)^k \frac{(2k-1)(2k-3)}{2k(2k-2)}\frac{x^{2k-3}}{(2k-4)!}\end{aligned} \tag{14.54}$$

The general expression, after a bit of messing around (and I got it wrong the first time), can be found to be

$$\begin{aligned}\left(\frac{1}{x}\frac{d}{dx}\right)^l-\frac{\cos x}{x} &= (-1)^{l+1}\sum_{k=0}^{l-1}\prod_{j=0}^{l-1}|2(k-j)-1|\frac{x^{2(k-l)-1}}{(2k)!} \\ &\quad + (-1)^{l+1}\sum_{k=0}^{\infty}(-1)^k \frac{(2(k+l)-1)!\,!}{(2k-1)!\,!}\frac{x^{2k-1}}{(2(k+l)!}.\end{aligned} \tag{14.55}$$

We really only need the lowest order term (which dominates for small x) to confirm the small limit eq. (14.28b) of the Neumann function, and this follows immediately.

For completeness, we note that the series expansion of the Neumann function is

$$\begin{aligned} n_l(x) = &- \sum_{k=0}^{l-1} \prod_{j=0}^{l-1} |2(k-j)-1| \frac{x^{2k-l-1}}{(2k)!} \\ &- \sum_{k=0}^{\infty} (-1)^k \frac{(2k+3l-1)!\,!}{(2k-1)!\,!} \frac{x^{2k-1}}{(2(k+l)!}. \end{aligned} \tag{14.56}$$

14.8 VERIFYING THE SOLUTION TO THE SPHERICAL BESSEL EQUATION

One way to verify that eq. (14.18a) is a solution to the Bessel equation eq. (14.17) as claimed should be to substitute the series expression and verify that we get zero. Another way is to solve this equation directly. We have a regular singular point at the origin, so we look for solutions of the form

$$f = x^r \sum_{k=0}^{\infty} a_k x^k \tag{14.57}$$

Writing our differential operator as

$$L = x^2 \frac{d^2}{dx^2} + 2x \frac{d}{dx} + x^2 - l(l+1), \tag{14.58}$$

we get

$$\begin{aligned} 0 &= Lf \\ &= \sum_{k=0}^{\infty} a_k \big((k+r)(k+r-1) + 2(k+r) - l(l+1)\big) x^{k+r} + a_k x^{k+r+2} \\ &= a_0 \big(r(r+1) - l(l+1)\big) x^r \\ &+ a_1 \big((r+1)(r+2) - l(l+1)\big) x^{r+1} \\ &+ \sum_{k=2}^{\infty} a_k \big((k+r)(k+r-1) + 2(k+r) - l(l+1) + a_{k-2}\big) x^{k+r} \end{aligned} \tag{14.59}$$

Since we require this to be zero for all x including non-zero values, we must have constraints on r. Assuming first that a_0 is non-zero we must then have

$$0 = r(r+1) - l(l+1). \tag{14.60}$$

One solution is obviously $r = l$. Assuming we have another solution $r = l + k$ for some integer k we find that $r = -l - 1$ is also a solution. Restricting attention first to $r = l$, we must have $a_1 = 0$ since for non-negative l we have $(l+1)(l+2) - l(l+1) = 2(l+1) \neq 0$. Thus for non-zero a_0 we find that our function is of the form

$$f = \sum_k a_{2k} x^{2k+l}. \tag{14.61}$$

It does not matter that we started with $a_0 \neq 0$. If we instead start with $a_1 \neq 0$ we find that we must have $r = l - 1, -l - 2$, so end up with exactly the same functional form as eq. (14.61). It ends up slightly simpler if we start with eq. (14.61) instead, since we now know that we do not have any odd powered a_k's to deal with. Doing so we find

$$\begin{aligned} 0 &= Lf \\ &= \sum_{k=0}^{\infty} a_{2k}\big((2k+l)(2k+l-1) + 2(2k+l) - l(l+1)\big)x^{2k+l} + a_{2k}x^{2k+l+2} \\ &= \sum_{k=1}^{\infty} \big(a_{2k} 2k(2(k+l)+1) + a_{2(k-1)}\big)x^{2k+l} \end{aligned} \tag{14.62}$$

We find

$$\frac{a_{2k}}{a_{2(k-1)}} = \frac{-1}{2k(2(k+l)+1)}. \tag{14.63}$$

Proceeding recursively, we find

$$f = a_0(2l+1)!\,! \sum_{k=0}^{\infty} \frac{(-1)^k}{(2k)!\,!\,(2(k+l)+1)!\,!} x^{2k+l}. \tag{14.64}$$

With $a_0 = 1/(2l+1)!\,!$ and the observation that

$$\frac{1}{(2k)!\,!} = \frac{(2k+1)!\,!}{(2k+1)!}, \tag{14.65}$$

we have $f = j_l(x)$ as given in eq. (14.53).
If we do the same for the $r = -l - 1$ case, we find

$$\frac{a_{2k}}{a_{2(k-1)}} = \frac{-1}{2k(2(k-l)-1)}, \tag{14.66}$$

and find

$$\frac{a_{2k}}{a_0} = \frac{(-1)^k}{(2k)!\,!\,(2(k-l)-1)(2(k-l)-3)\cdots(-2l+1)}. \tag{14.67}$$

Flipping signs around, we can rewrite this as

$$\frac{a_{2k}}{a_0} = \frac{1}{(2k)!\,!\,(2(l-k)+1)(2(l-k)+3)\cdots(2l-1)}. \tag{14.68}$$

For those values of $l > k$ we can write this as

$$\frac{a_{2k}}{a_0} = \frac{(2(l-k)-1)!\,!}{(2k)!\,!\,(2l-1)!\,!}. \tag{14.69}$$

Comparing to the small limit eq. (14.28b), the $k = 0$ term, we find that we must have

$$\frac{a_0}{(2l-1)!\,!} = -1. \tag{14.70}$$

After some play we find

$$a_{2k} = \begin{cases} -\frac{(2(l-k)-1)!!}{(2k)!!} & \text{if } l \geq k \\ \frac{(-1)^{k-l+1}}{(2k)!!(2(k-l)-1)!!} & \text{if } l \leq k \end{cases} \tag{14.71}$$

Putting this all together we have

$$n_l(x) = -\sum_{0 \leq k \leq l} (2(l-k)-1)!\,!\,\frac{x^{2k-l-1}}{(2k)!\,!} - \sum_{l<k} \frac{(-1)^{k-l}}{(2(k-l)-1)!\,!}\frac{x^{2k-l-1}}{(2k)!\,!} \tag{14.72}$$

FIXME: check that this matches the series calculated earlier eq. (14.56).

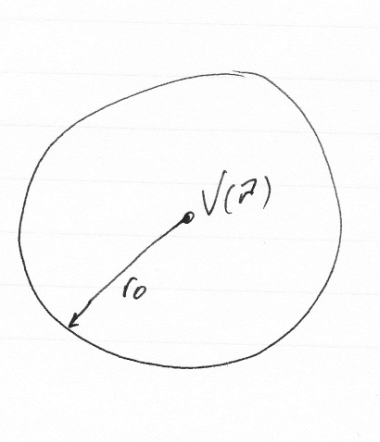

Figure 14.4: Bounded potential

14.9 SCATTERING CROSS SECTIONS

READING: §20 [4]

Recall that we are studing the case of a potential that is zero outside of a fixed bound, $V(\mathbf{r}) = 0$ for $r > r_0$, as in fig. 14.4

and were looking for solutions to Schrödinger's equation

$$-\frac{\hbar^2}{2\mu}\boldsymbol{\nabla}^2\psi_{\mathbf{k}}(\mathbf{r}) + V(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r}) = \frac{\hbar^2\mathbf{k}^2}{2\mu}\psi_{\mathbf{k}}(\mathbf{r}), \tag{14.73}$$

in regions of space, where $r > r_0$ is very large. We found

$$\psi_{\mathbf{k}}(\mathbf{r}) \sim e^{i\mathbf{k}\cdot\mathbf{r}} + \frac{e^{ikr}}{r} f_{\mathbf{k}}(\theta, \phi). \tag{14.74}$$

For $r \leq r_0$ this will be something much more complicated.

To study scattering we will use the concept of probability flux as in electromagnetism

$$\boldsymbol{\nabla}\cdot\mathbf{j} + \dot{\rho} = 0 \tag{14.75}$$

Using

$$\psi(\mathbf{r}, t) = \psi_{\mathbf{k}}(\mathbf{r})^*\psi_{\mathbf{k}}(\mathbf{r}) \tag{14.76}$$

we find

$$\mathbf{j}(\mathbf{r},t) = \frac{\hbar}{2\mu i}\left(\psi_{\mathbf{k}}(\mathbf{r})^*\boldsymbol{\nabla}\psi_{\mathbf{k}}(\mathbf{r}) - (\boldsymbol{\nabla}\psi^*_{\mathbf{k}}(\mathbf{r}))\psi_{\mathbf{k}}(\mathbf{r})\right) \tag{14.77}$$

when

$$-\frac{\hbar^2}{2\mu}\boldsymbol{\nabla}^2\psi_{\mathbf{k}}(\mathbf{r}) + V(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r}) = i\hbar\frac{\partial\psi_{\mathbf{k}}(\mathbf{r})}{\partial t} \tag{14.78}$$

In a fashion similar to what we did in the 1D case, let us suppose that we can write our wave function

$$\psi(\mathbf{r},t_{\text{initial}}) = \int d^3k\alpha(\mathbf{k},t_{\text{initial}})\psi_{\mathbf{k}}(\mathbf{r}) \tag{14.79}$$

and treat the scattering as the scattering of a plane wave front (idealizing a set of wave packets) off of the object of interest as depicted in fig. 14.5

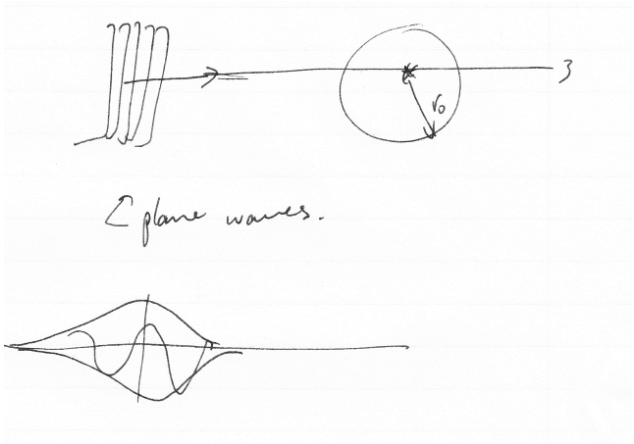

Figure 14.5: plane wave front incident on particle

We assume that our incoming particles are sufficiently localized in k space as depicted in the idealized representation of fig. 14.6

we assume that $\alpha(\mathbf{k},t_{\text{initial}})$ is localized.

$$\psi(\mathbf{r},t_{\text{initial}}) = \int d^3k\left(\alpha(\mathbf{k},t_{\text{initial}})e^{ik_z z} + \alpha(\mathbf{k},t_{\text{initial}})\frac{e^{ikr}}{r}f_{\mathbf{k}}(\theta,\phi)\right) \tag{14.80}$$

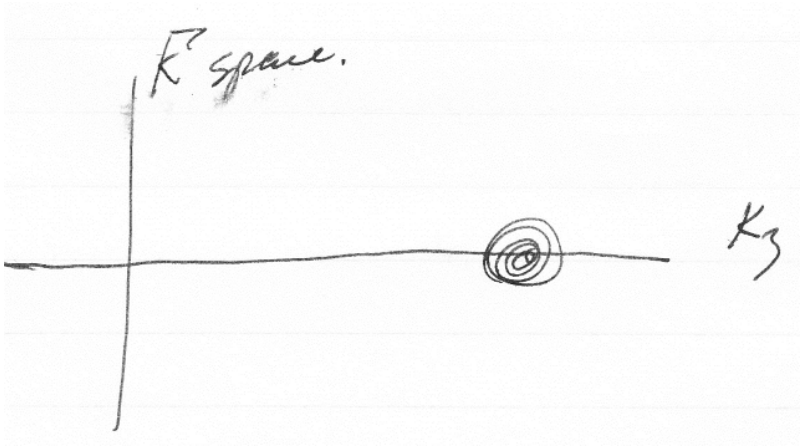

Figure 14.6: k space localized wave packet

We suppose that

$$\alpha(\mathbf{k}, t_{\text{initial}}) = \alpha(\mathbf{k}) e^{-i\hbar k^2 t_{\text{initial}}/2\mu} \tag{14.81}$$

where this is chosen ($\alpha(\mathbf{k}, t_{\text{initial}})$ is built in this fashion) so that this is non-zero for z large in magnitude and negative.

This last integral can be approximated

$$\begin{aligned}\int d^3k \alpha(\mathbf{k}, t_{\text{initial}}) \frac{e^{ikr}}{r} f_{\mathbf{k}}(\theta, \phi) &\approx \frac{f_{\mathbf{k}_0}(\theta, \phi)}{r} \int d^3k \alpha(\mathbf{k}, t_{\text{initial}}) e^{ikr} \\ &\to 0\end{aligned} \tag{14.82}$$

This is very much like the 1D case where we found no reflected component for our initial time.

We will normally look in a locality well away from the wave front as indicted in fig. 14.7

There are situations where we do look in the locality of the wave front that has been scattered.

Incoming wave Our income wave is of the form

$$\psi_i = A e^{ikz} e^{-i\hbar k^2 t/2\mu} \tag{14.83}$$

Here we have made the approximation that $k = |\mathbf{k}| \sim k_z$. We can calculate the probability current

$$\mathbf{j} = \hat{\mathbf{z}} \frac{\hbar k}{\mu} A \tag{14.84}$$

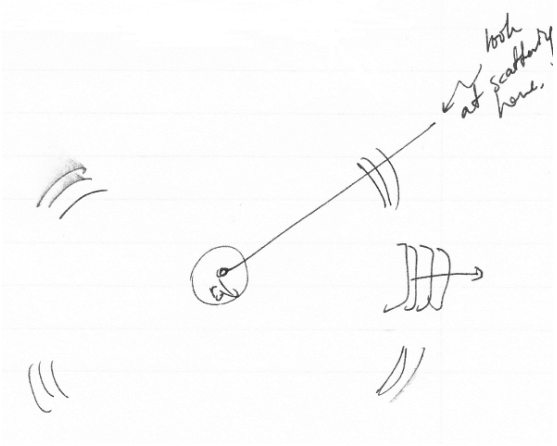

Figure 14.7: point of measurement of scattering cross section

(notice the $v = p/m$ like term above, with $p = \hbar k$).
For the scattered wave (dropping A factor)

$$\begin{aligned}\mathbf{j} &= \frac{\hbar}{2\mu i}\left(f^*_{\mathbf{k}}(\theta,\phi)\frac{e^{-ikr}}{r}\boldsymbol{\nabla}\left(f_{\mathbf{k}}(\theta,\phi)\frac{e^{ikr}}{r}\right) - \boldsymbol{\nabla}\left(f^*_{\mathbf{k}}(\theta,\phi)\frac{e^{-ikr}}{r}\right)f_{\mathbf{k}}(\theta,\phi)\frac{e^{ikr}}{r}\right) \\ &\approx \frac{\hbar}{2\mu i}\left(f^*_{\mathbf{k}}(\theta,\phi)\frac{e^{-ikr}}{r}ik\hat{\mathbf{r}}f_{\mathbf{k}}(\theta,\phi)\frac{e^{ikr}}{r} - f^*_{\mathbf{k}}(\theta,\phi)\frac{e^{-ikr}}{r}(-ik\hat{\mathbf{r}})f_{\mathbf{k}}(\theta,\phi)\frac{e^{ikr}}{r}\right)\end{aligned} \tag{14.85}$$

We find that the radial portion of the current density is

$$\begin{aligned}\hat{\mathbf{r}}\cdot\mathbf{j} &= \frac{\hbar}{2\mu i}|f|^2\frac{2ik}{r^2} \\ &= \frac{\hbar k}{\mu}\frac{1}{r^2}|f|^2,\end{aligned} \tag{14.86}$$

and the flux through our element of solid angle is

$$\begin{aligned}\hat{\mathbf{r}}dA\cdot\mathbf{j} &= \frac{\text{probability}}{\text{unit area per time}}\times\text{area}\\ &= \frac{\text{probability}}{\text{unit time}}\\ &= \frac{\hbar k}{\mu}\frac{|f_{\mathbf{k}}(\theta,\phi)|^2}{r^2}r^2d\Omega\\ &= \frac{\hbar k}{\mu}|f_{\mathbf{k}}(\theta,\phi)|^2d\Omega\\ &= j_{\text{incoming}}\underbrace{|f_{\mathbf{k}}(\theta,\phi)|^2}_{d\sigma/d\Omega}d\Omega.\end{aligned} \tag{14.87}$$

We identify the scattering cross section above

$$\frac{d\sigma}{d\Omega} = |f_{\mathbf{k}}(\theta,\phi)|^2 \tag{14.88}$$

$$\sigma = \int |f_{\mathbf{k}}(\theta,\phi)|^2 d\Omega \tag{14.89}$$

We have been somewhat unrealistic here since we have used a plane wave approximation, and can as in fig. 14.8

will actually produce the same answer. For details we are referred to [10] and [12].

Working towards a solution We have done a bunch of stuff here but are not much closer to a real solution because we do not actually know what $f_{\mathbf{k}}$ is.

Let us write Schrödinger

$$-\frac{\hbar^2}{2\mu}\boldsymbol{\nabla}^2\psi_{\mathbf{k}}(\mathbf{r}) + V(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r}) = \frac{\hbar^2\mathbf{k}^2}{2\mu}\psi_{\mathbf{k}}(\mathbf{r}), \tag{14.90}$$

instead as

$$(\boldsymbol{\nabla}^2 + \mathbf{k}^2)\psi_{\mathbf{k}}(\mathbf{r}) = s(\mathbf{r}) \tag{14.91}$$

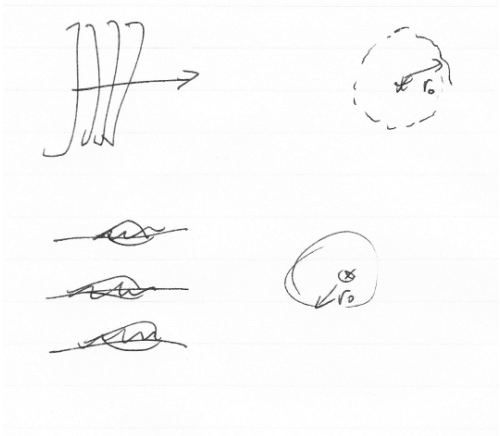

Figure 14.8: Plane wave vs packet wave front

where

$$s(\mathbf{r}) = \frac{2\mu}{\hbar^2} V(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r}) \tag{14.92}$$

where $s(\mathbf{r})$ is really the particular solution to this differential problem. We want

$$\psi_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}}^{\text{homogeneous}}(\mathbf{r}) + \psi_{\mathbf{k}}^{\text{particular}}(\mathbf{r}) \tag{14.93}$$

and

$$\psi_{\mathbf{k}}^{\text{homogeneous}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \tag{14.94}$$

15

BORN APPROXIMATION

READING: §20 [4]

We have been arguing that we can write the stationary equation

$$\left(\boldsymbol{\nabla}^2 + \mathbf{k}^2\right)\psi_{\mathbf{k}}(\mathbf{r}) = s(\mathbf{r}) \tag{15.1}$$

with

$$s(\mathbf{r}) = \frac{2\mu}{\hbar^2}V(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r}) \tag{15.2}$$

$$\psi_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}}^{\text{homogeneous}}(\mathbf{r}) + \psi_{\mathbf{k}}^{\text{particular}}(\mathbf{r}) \tag{15.3}$$

Introduce Green function

$$\left(\boldsymbol{\nabla}^2 + \mathbf{k}^2\right)G^0(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \tag{15.4}$$

Suppose that I can find $G^0(\mathbf{r}, \mathbf{r}')$, then

$$\psi_{\mathbf{k}}^{\text{particular}}(\mathbf{r}) = \int G^0(\mathbf{r}, \mathbf{r}')s(\mathbf{r}')d^3\mathbf{r}' \tag{15.5}$$

It turns out that finding the Green's function $G^0(\mathbf{r}, \mathbf{r}')$ is not so hard. Note the following, for $k = 0$, we have

$$\boldsymbol{\nabla}^2 G_0^0(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \tag{15.6}$$

(where a zero subscript is used to mark the $k = 0$ case). We know this Green's function from electrostatics, and conclude that

$$G_0^0(\mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi}\frac{1}{|\mathbf{r} - \mathbf{r}'|} \tag{15.7}$$

For $\mathbf{r} \neq \mathbf{r}'$ we can easily show that

$$G^0(\mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi} \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \tag{15.8}$$

This is correct for all $\mathbf{r}$ because it also gives the right limit as $\mathbf{r} \to \mathbf{r}'$. This argument was first given by Lorentz. An outline for a derivation, utilizing the usual Fourier transform and contour integration arguments for these Green's derivations, can be found in §7.4 of [3]. A direct verification, not quite as easy as claimed can be found in B.

We can now write our particular solution

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{1}{4\pi} \int \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} s(\mathbf{r}') d^3\mathbf{r}' \tag{15.9}$$

This is of no immediate help since we do not know $\psi_{\mathbf{k}}(\mathbf{r})$ and that is embedded in $s(\mathbf{r})$.

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{2\mu}{4\pi\hbar^2} \int \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} V(\mathbf{r}') \psi_{\mathbf{k}}(\mathbf{r}') d^3\mathbf{r}' \tag{15.10}$$

Now look at this for $\mathbf{r} \gg \mathbf{r}'$

$$\begin{aligned} \left|\mathbf{r}-\mathbf{r}'\right| &= \left(\mathbf{r}^2 + (\mathbf{r}')^2 - 2\mathbf{r}\cdot\mathbf{r}'\right)^{1/2} \\ &= r\left(1 + \frac{(\mathbf{r}')^2}{\mathbf{r}^2} - 2\frac{1}{\mathbf{r}^2}\mathbf{r}\cdot\mathbf{r}'\right)^{1/2} \\ &= r\left(1 - \frac{1}{2}\frac{2}{\mathbf{r}^2}\mathbf{r}\cdot\mathbf{r}' + O\left(\frac{r'}{r}\right)^2\right)^{1/2} \\ &= r - \hat{\mathbf{r}}\cdot\mathbf{r}' + O\left(\frac{r'^2}{r}\right) \end{aligned} \tag{15.11}$$

We get

$$\begin{aligned} \psi_{\mathbf{k}}(\mathbf{r}) &\to e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{2\mu}{4\pi\hbar^2} \frac{e^{ikr}}{r} \int e^{-ik\hat{\mathbf{r}}\cdot\mathbf{r}'} V(\mathbf{r}') \psi_{\mathbf{k}}(\mathbf{r}') d^3\mathbf{r}' \\ &= e^{i\mathbf{k}\cdot\mathbf{r}} + f_{\mathbf{k}}(\theta,\phi)\frac{e^{ikr}}{r}, \end{aligned} \tag{15.12}$$

where

$$f_{\mathbf{k}}(\theta,\phi) = -\frac{\mu}{2\pi\hbar^2} \int e^{-ik\hat{\mathbf{r}}\cdot\mathbf{r}'} V(\mathbf{r}') \psi_{\mathbf{k}}(\mathbf{r}') d^3\mathbf{r}' \tag{15.13}$$

If the scattering is weak we have the Born approximation

$$f_{\mathbf{k}}(\theta,\phi) = -\frac{\mu}{2\pi\hbar^2}\int e^{-ik\hat{\mathbf{r}}\cdot\mathbf{r}'}V(\mathbf{r}')e^{i\mathbf{k}\cdot\mathbf{r}'}d^3\mathbf{r}', \tag{15.14}$$

or

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{\mu}{2\pi\hbar^2}\frac{e^{ikr}}{r}\int e^{-ik\hat{\mathbf{r}}\cdot\mathbf{r}'}V(\mathbf{r}')e^{i\mathbf{k}\cdot\mathbf{r}'}d^3\mathbf{r}'. \tag{15.15}$$

Should we wish to make a further approximation, we can take the wave function resulting from application of the Born approximation, and use that a second time. This gives us the "Born again" approximation of

$$\begin{aligned}\psi_{\mathbf{k}}(\mathbf{r}) &= e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{\mu}{2\pi\hbar^2}\frac{e^{ikr}}{r}\int e^{-ik\hat{\mathbf{r}}\cdot\mathbf{r}'}V(\mathbf{r}')\left(e^{i\mathbf{k}\cdot\mathbf{r}'} - \frac{\mu}{2\pi\hbar^2}\frac{e^{ikr'}}{r'}\int e^{-ik\hat{\mathbf{r}}'\cdot\mathbf{r}''}V(\mathbf{r}'')e^{i\mathbf{k}\cdot\mathbf{r}''}d^3\mathbf{r}''\right)d^3\mathbf{r}' \\ &= e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{\mu}{2\pi\hbar^2}\frac{e^{ikr}}{r}\int e^{-ik\hat{\mathbf{r}}\cdot\mathbf{r}'}V(\mathbf{r}')e^{i\mathbf{k}\cdot\mathbf{r}'}d^3\mathbf{r}' \\ &\quad + \frac{\mu^2}{(2\pi)^2\hbar^4}\frac{e^{ikr}}{r}\int e^{-ik\hat{\mathbf{r}}\cdot\mathbf{r}'}V(\mathbf{r}')\frac{e^{ikr'}}{r'}\int e^{-ik\hat{\mathbf{r}}'\cdot\mathbf{r}''}V(\mathbf{r}'')e^{i\mathbf{k}\cdot\mathbf{r}''}d^3\mathbf{r}''d^3\mathbf{r}'.\end{aligned} \tag{15.16}$$

Part IV

NOTES AND PROBLEMS

16

SIMPLE ENTANGLEMENT EXAMPLE

On the quiz we were given a three state system $|1\rangle, |2\rangle$ and $|3\rangle$, and a two state system $|a\rangle, |b\rangle$, and were asked to show that the composite system can be entangled. I had trouble with this, having not seen any examples of this and subsequently filing away entanglement in the "abstract stuff that has no current known application" bit bucket, and then forgetting about it. Let us generate a concrete example of entanglement, and consider the very simplest direct product spaces.

What is the simplest composite state that we can create? Suppose we have a pair of two state systems, say,

$$\begin{aligned} |1\rangle &= \begin{bmatrix} 1 \\ 0 \end{bmatrix} \in H_1 \\ |2\rangle &= \begin{bmatrix} 0 \\ 1 \end{bmatrix} \in H_1, \end{aligned} \tag{16.1}$$

and

$$\begin{aligned} \langle x|+\rangle &= \frac{e^{ikx}}{\sqrt{2\pi}}, \text{where } |+\rangle \in H_2 \\ \langle x|+\rangle &= \frac{e^{-ikx}}{\sqrt{2\pi}} \text{where } |-\rangle \in H_2. \end{aligned} \tag{16.2}$$

We can now enumerate the space of possible operators

$$\begin{aligned} A \in\ & a_{11++} |1\rangle\langle 1| \otimes |+\rangle\langle +| + a_{11+-} |1\rangle\langle 1| \otimes |+\rangle\langle -| \\ & + a_{11-+} |1\rangle\langle 1| \otimes |-\rangle\langle +| + a_{11--} |1\rangle\langle 1| \otimes |-\rangle\langle -| \\ & + a_{12++} |1\rangle\langle 2| \otimes |+\rangle\langle +| + a_{12+-} |1\rangle\langle 2| \otimes |+\rangle\langle -| \\ & + a_{12-+} |1\rangle\langle 2| \otimes |-\rangle\langle +| + a_{12--} |1\rangle\langle 2| \otimes |-\rangle\langle -| \\ & + a_{21++} |2\rangle\langle 1| \otimes |+\rangle\langle +| + a_{21+-} |2\rangle\langle 1| \otimes |+\rangle\langle -| \\ & + a_{21-+} |2\rangle\langle 1| \otimes |-\rangle\langle +| + a_{21--} |2\rangle\langle 1| \otimes |-\rangle\langle -| \\ & + a_{22++} |2\rangle\langle 2| \otimes |+\rangle\langle +| + a_{22+-} |2\rangle\langle 2| \otimes |+\rangle\langle -| \\ & + a_{22-+} |2\rangle\langle 2| \otimes |-\rangle\langle +| + a_{22--} |2\rangle\langle 2| \otimes |-\rangle\langle -| \end{aligned} \tag{16.3}$$

We can also enumerate all the possible states, some of these can be entangled

$$|\psi\rangle \in h_{1+}\,|1\rangle \otimes |+\rangle + h_{1-}\,|1\rangle \otimes |-\rangle + h_{2+}\,|2\rangle \otimes |+\rangle + h_{2-}\,|2\rangle \otimes |-\rangle\,. \tag{16.4}$$

And finally, we can enumerate all the possible product states

$$|\psi\rangle \in (a_i\,|i\rangle) \otimes (b_\beta\,|\beta\rangle) = a_1 b_+\,|1\rangle \otimes |+\rangle + a_1 b_-\,|1\rangle \otimes |-\rangle + a_2 b_+\,|2\rangle \otimes |+\rangle + a_2 b_-\,|2\rangle \otimes |-\rangle \tag{16.5}$$

In this simpler example, we have the same dimensionality for both the sets of direct product kets and the ones formed by arbitrary superposition of the composite ket basis elements, but that does not mean that this rules out entanglement.

Suppose that, as the product of some operator, we end up with a ket

$$|\psi\rangle = |1\rangle \otimes |+\rangle + |2\rangle \otimes |-\rangle \tag{16.6}$$

Does this have a product representation, of the following form

$$|\psi\rangle = (a_i\,|i\rangle) \otimes (b_\beta\,|\beta\rangle) = a_i b_\beta\,|i\rangle \otimes |\beta\rangle\,? \tag{16.7}$$

For this to be true we would require

$$\begin{aligned} a_1 b_+ &= 1 \\ a_2 b_- &= 1 \\ a_1 b_- &= 0 \\ a_2 b_+ &= 0, \end{aligned} \tag{16.8}$$

However, we can not find a solution to this set of equations. We require one of $a_1 = 0$ or $b_- = 0$ for the third equality, but such zeros generate contradictions for one of the first pair of equations.

17

PROBLEM SET 4, PROBLEM 2 NOTES

I was deceived by an incorrect result in Mathematica, which led me to believe that the second order energy perturbation was zero (whereas part (c) of the problem asked if it was greater or lesser than zero). I started starting writing this up to show my reasoning, but our Professor quickly provided an example after class showing how this zero must be wrong, and I did not have to show him any of this.

Setup Recall first the one dimensional particle in a box. Within the box we have to solve

$$\frac{P^2}{2m}\psi = E\psi \tag{17.1}$$

and find

$$\psi \sim e^{\frac{i}{\hbar}\sqrt{2mE}x} \tag{17.2}$$

With

$$k = \frac{\sqrt{2mE}}{\hbar} \tag{17.3}$$

our general state, involving terms of each sign, takes the form

$$\psi = Ae^{ikx} + Be^{-ikx} \tag{17.4}$$

Inserting boundary conditions gives us

$$\begin{bmatrix} \psi(-L/2) \\ \psi(L/2) \end{bmatrix} \begin{bmatrix} e^{-ik\frac{L}{2}} + e^{ik\frac{L}{2}} \\ e^{ik\frac{L}{2}} + e^{-ik\frac{L}{2}} \end{bmatrix} \begin{bmatrix} A \\ B \end{bmatrix} \tag{17.5}$$

The determinant is zero

$$e^{-ikL} - e^{ikL} = 0, \tag{17.6}$$

which provides our constraint on k

$$e^{2ikL} = 1. \tag{17.7}$$

We require $2kL = 2\pi n$ for any integer n, or

$$k = \frac{\pi n}{L}. \tag{17.8}$$

This quantizes the energy, and inverting eq. (17.3) gives us

$$E = \frac{1}{2m}\left(\frac{\hbar\pi n}{L}\right)^2. \tag{17.9}$$

To complete the task of matching boundary value conditions we cheat and recall that the particular linear combinations that we need to match the boundary constraint of zero at $\pm L/2$ were sums and differences yielding cosines and sines respectively. Since

$$\sin\left(\frac{\pi n x}{L}\right)\Big|_{x=\pm L/2} = \pm\sin\left(\frac{\pi n}{2}\right) \tag{17.10}$$

So sines are the wave functions for $n = 2, 4, ...$ since $\sin(n\pi) = 0$ for integer n. Similarly

$$\cos\left(\frac{\pi n x}{L}\right)\Big|_{x=\pm L/2} = \cos\left(\frac{\pi n}{2}\right). \tag{17.11}$$

Cosine becomes zero at $\pi/2, 3\pi/2, \cdots$, so our wave function is the cosine for $n = 1, 3, 5, \cdots$. Normalizing gives us

$$\psi_n(x) = \sqrt{\frac{2}{L}}\begin{cases} \cos\left(\frac{\pi n x}{L}\right) & n = 1, 3, 5, \cdots \\ \sin\left(\frac{\pi n x}{L}\right) & n = 2, 4, 6, \cdots \end{cases} \tag{17.12}$$

Two non-interacting particles. Three lowest energy levels and degeneracies Forming the Hamiltonian for two particles in the box without interaction, we have within the box

$$H = \frac{P_1^2}{2m} + \frac{P_2^2}{2m} \tag{17.13}$$

we can apply separation of variables, and it becomes clear that our wave functions have the form

$$\psi_{nm}(x_1, x_2) = \psi_n(x_1)\psi_m(x_2) \tag{17.14}$$

Plugging in

$$H\psi = E\psi, \tag{17.15}$$

supplies the energy levels for the two particle wavefunction, giving

$$\begin{aligned} H\psi_{nm} &= \frac{\hbar^2}{2m}\left(\left(\frac{\pi n}{L}\right)^2 + \left(\frac{\pi m}{L}\right)^2\right)\psi_{nm} \\ &= \frac{1}{2m}\left(\frac{\hbar\pi}{L}\right)^2 (n^2 + m^2)\psi_{nm} \end{aligned} \tag{17.16}$$

Letting n, m each range over $[1, 3]$ for example we find

$$\begin{array}{cc|c} n & m & n^2 + m^2 \\ 1 & 1 & 2 \\ 1 & 2 & 5 \\ 1 & 3 & 10 \\ 2 & 1 & 5 \\ 2 & 2 & 8 \\ 2 & 3 & 13 \\ 3 & 1 & 10 \\ 3 & 2 & 13 \\ 3 & 3 & 18 \end{array} \tag{17.17}$$

It is clear that our lowest energy levels are

$$\begin{aligned} &\frac{1}{m}\left(\frac{\hbar\pi}{L}\right)^2 \\ &\frac{5}{2m}\left(\frac{\hbar\pi}{L}\right)^2 \\ &\frac{4}{m}\left(\frac{\hbar\pi}{L}\right)^2 \end{aligned} \tag{17.18}$$

with degeneracies $1, 2, 1$ respectively.

Ground state energy with interaction perturbation to first order With c_0 positive and an interaction potential of the form

$$U(X_1, X_2) = -c_0 \delta(X_1 - X_2) \tag{17.19}$$

The second order perturbation of the ground state energy is

$$E = E_{11}^{(0)} + H'_{11;11} + \sum_{nm \neq 11} \frac{\left|H'_{11;11}\right|^2}{E_{11} - E_{nm}} \tag{17.20}$$

where

$$E_{11}^{(0)} = \frac{1}{m}\left(\frac{\hbar\pi}{L}\right)^2, \tag{17.21}$$

and

$$H'_{nm;ab} = -c_0 \langle \psi_{nm} | \, \delta(X_1 - X_2) \, | \psi_{ab} \rangle \tag{17.22}$$

to proceed, we need to expand the matrix element

$$\begin{aligned}
\langle \psi_{nm} | \, \delta(X_1 - X_2) \, | \psi_{ab} \rangle &= \int dx_1 dx_2 dy_1 dy_2 \, \langle \psi_{nm} | x_1 x_2 \rangle \, \langle x_1 x_2 | \, \delta(X_1 - X_2) \, | y_1 y_2 \rangle \, \langle y_1 y_2 | \psi_{ab} \rangle \\
&= \int dx_1 dx_2 dy_1 dy_2 \, \langle \psi_{nm} | x_1 x_2 \rangle \, \delta(x_1 - x_2) \delta^2(\mathbf{x} - \mathbf{y}) \, \langle y_1 y_2 | \psi_{ab} \rangle \\
&= \int dx_1 dx_2 \, \langle \psi_{nm} | x_1 x_2 \rangle \, \delta(x_1 - x_2) \, \langle x_1 x_2 | \psi_{ab} \rangle \\
&= \int_{-L/2}^{L/2} dx \psi_{nm}(x, x) \psi_{ab}(x, x)
\end{aligned} \tag{17.23}$$

So, for our first order calculation we need

$$\begin{aligned}
H'_{11;11} &= -c_0 \int_{-L/2}^{L/2} dx \psi_{11}(x, x) \psi_{11}(x, x) \\
&= \frac{4}{L^2} \int_{-L/2}^{L/2} dx \cos^4(\pi x / L) \\
&= -\frac{3c_0}{2L}
\end{aligned} \tag{17.24}$$

For the second order perturbation of the energy, it is clear that this will reduce the first order approximation for each matrix element that is non-zero.

Attempting that calculation with Mathematica however, is deceiving, since Mathematica reports these all as zero after FullSimplify. It appears, that as used, it does not allow for $m = n$ and $m = n \pm 1$ constraints properly where the denominators of the unsimplified integrals go zero.

This worksheet can be seen to be giving misleading results, by evaluating

$$\int_{-\frac{L}{2}}^{\frac{L}{2}} \left(\frac{2}{L}\right)^2 \cos^2\left(\frac{\pi x}{L}\right) \cos^2\left(\frac{3\pi x}{L}\right) dx = \frac{1}{L} \tag{17.25}$$

Yet, the FullSimplify gives

$$\text{FullSimplify}\left[\int_{-\frac{L}{2}}^{\frac{L}{2}} \text{Cos}\left[\frac{\pi x}{L}\right]^2 \left(\frac{2}{L}\right)^2 \text{Cos}\left[\frac{(2n+1)\pi x}{L}\right] \text{Cos}\left[\frac{(2m+1)\pi x}{L}\right] dx, \{m, n\} \in \text{Integers}\right] = 0 \tag{17.26}$$

I am hoping that asking about this on stackoverflow will clarify how to use Mathematica correctly for this calculation.

18

A DIFFERENT DERIVATION OF THE ADIABATIC PERTURBATION COEFFICIENT EQUATION

Professor Sipe's adiabatic perturbation and that of the text [4] in §17.5.1 and §17.5.2 use different notation for γ_m and take a slightly different approach. We can find Prof Sipe's final result with a bit less work, if a hybrid of the two methods is used.

Our starting point is the same, we have a time dependent slowly varying Hamiltonian

$$H = H(t), \tag{18.1}$$

where our perturbation starts at some specific time from a given initial state

$$H(t) = H_0, \qquad t \leq 0. \tag{18.2}$$

We assume that instantaneous eigenkets can be found, satisfying

$$H(t)\,|n(t)\rangle = E_n(t)\,|n(t)\rangle \tag{18.3}$$

Here I will use $|n\rangle \equiv |n(t)\rangle$ instead of the $\left|\hat{\psi}_n(t)\right\rangle$ that we used in class because its easier to write.

Now suppose that we have some arbitrary state, expressed in terms of the instantaneous basis kets $|n\rangle$

$$|\psi\rangle = \sum_n \bar{b}_n(t) e^{-i\alpha_n + i\beta_n}\,|n\rangle\,, \tag{18.4}$$

where

$$\alpha_n(t) = \frac{1}{\hbar}\int_0^t dt' E_n(t'). \tag{18.5}$$

Here I have used β_n instead of γ_n (as in the text) to avoid conflicting with the lecture notes, where this β_n is a factor to be determined.

For this state, we have at the time just before the perturbation

$$|\psi(0)\rangle = \sum_n \bar{b}_n(0) e^{-i\alpha_n(0)+i\beta_n(0)} |n(0)\rangle . \tag{18.6}$$

The question to answer is: How does this particular state evolve?

Another question, for those that do not like sneaky bastard derivations, is where did that magic factor of $e^{-i\alpha_n}$ come from in our superposition state? We will see after we start taking derivatives that this is what we need to cancel the $H(t)|n\rangle$ in Schrödinger's equation.

Proceeding to plug into the evolution identity we have

$$\begin{aligned}
0 &= \langle m| \left(i\hbar \frac{d}{dt} - H(t) \right) |\psi\rangle \\
&= \langle m| \left(\sum_n e^{-i\alpha_n+i\beta_n} (i\hbar) \left(\frac{d\bar{b}_n}{dt} + \bar{b}_n \left(-i\frac{\cancel{E_n}}{\cancel{\hbar}} + i\dot{\beta}_m \right) \right) |n\rangle + i\hbar \bar{b}_n \frac{d}{dt} |n\rangle - \cancel{E_n \bar{b}_n |n\rangle} \right) \\
&= e^{-i\alpha_m+i\beta_m} (i\hbar) \frac{d\bar{b}_m}{dt} + e^{-i\alpha_m+i\beta_m} (i\hbar) i\dot{\beta}_m \bar{b}_m + i\hbar \sum_n \bar{b}_n \langle m| \frac{d}{dt} |n\rangle e^{-i\alpha_n+i\beta_n} \\
&\sim \frac{d\bar{b}_m}{dt} + i\dot{\beta}_m \bar{b}_m + \sum_n e^{-i\alpha_n+i\beta_n} e^{i\alpha_m-i\beta_m} \bar{b}_n \langle m| \frac{d}{dt} |n\rangle \\
&= \frac{d\bar{b}_m}{dt} + i\dot{\beta}_m \bar{b}_m + \bar{b}_m \langle m| \frac{d}{dt} |m\rangle + \sum_{n\neq m} e^{-i\alpha_n+i\beta_n} e^{i\alpha_m-i\beta_m} \bar{b}_n \langle m| \frac{d}{dt} |n\rangle
\end{aligned} \tag{18.7}$$

We are free to pick β_m to kill the second and third terms

$$0 = i\dot{\beta}_m \bar{b}_m + \bar{b}_m \langle m| \frac{d}{dt} |m\rangle , \tag{18.8}$$

or

$$\dot{\beta}_m = i \langle m| \frac{d}{dt} |m\rangle , \tag{18.9}$$

which after integration is

$$\beta_m(t) = i \int_0^t dt' \left\langle m(t') \right| \frac{d}{dt'} |m(t)\rangle . \tag{18.10}$$

In the lecture notes this was written as

$$\Gamma_m(t) = i \langle m(t)| \frac{d}{dt} |m(t)\rangle \tag{18.11}$$

so that

$$\beta_m(t) = \int_0^t dt' \Gamma_m(t'). \tag{18.12}$$

As in class we can observe that this is a purely real function. We are left with

$$\frac{d\bar{b}_m}{dt} = -\sum_{n\neq m} \bar{b}_n e^{-i\alpha_{nm}+i\beta_{nm}} \langle m| \frac{d}{dt} |n\rangle , \tag{18.13}$$

where

$$\begin{aligned} \alpha_{nm} &= \alpha_n - \alpha_m \\ \beta_{nm} &= \beta_n - \beta_m \end{aligned} \tag{18.14}$$

The task is now to find solutions for these $\bar{b}_m$ coefficients, and we can refer to the class notes for that without change.

19

SECOND ORDER TIME EVOLUTION FOR THE COEFFICIENTS OF AN INITIALLY PURE KET WITH AN ADIABATICALLY CHANGING HAMILTONIAN

Motivation In lecture 9, Prof Sipe developed the equations governing the evolution of the coefficients of a given state for an adiabatically changing Hamiltonian. He also indicated that we could do an approximation, finding the evolution of an initially pure state in powers of λ (like we did for the solutions of a non-time dependent perturbed Hamiltonian $H = H_0 + \lambda H'$). I tried doing that a couple of times and always ended up going in circles. I will show that here and also develop an expansion in time up to second order as an alternative, which appears to work out nicely.

Review We assumed that an adiabatically changing Hamiltonian was known with instantaneous eigenkets governed by

$$H(t)\left|\hat{\psi}_n(t)\right\rangle = \hbar\omega_n\left|\hat{\psi}_n(t)\right\rangle \tag{19.1}$$

The problem was to determine the time evolutions of the coefficients $\bar{b}_n(t)$ of some state $|\psi(t)\rangle$, and this was found to be

$$\begin{aligned}
|\psi(t)\rangle &= \sum_n \bar{b}_n(t)e^{-i\gamma_n(t)}\left|\hat{\psi}_n(t)\right\rangle \\
\gamma_s(t) &= \int_0^t dt'(\omega_s(t') - \Gamma_s(t')) \\
\Gamma_s(t) &= i\left\langle\hat{\psi}_s(t)\right|\frac{d}{dt}\left|\hat{\psi}_s(t)\right\rangle
\end{aligned} \tag{19.2}$$

where the $\bar{b}_s(t)$ coefficient must satisfy the set of LDEs

$$\frac{d\bar{b}_s(t)}{dt} = -\sum_{n\neq s}\bar{b}_n(t)e^{i\gamma_{sn}(t)}\left\langle\hat{\psi}_s(t)\right|\frac{d}{dt}\left|\hat{\psi}_n(t)\right\rangle, \tag{19.3}$$

where

$$\gamma_{sn}(t) = \gamma_s(t) - \gamma_n(t). \tag{19.4}$$

Solving these in general does not look terribly fun, but perhaps we can find an explicit solution for all the $\bar{b}_s$'s, if we simplify the problem somewhat. Suppose that our initial state is found to be in the mth energy level at the time before we start switching on the changing Hamiltonian.

$$|\psi(0)\rangle = \bar{b}_m(0) \left|\hat{\psi}_m(0)\right\rangle. \tag{19.5}$$

We therefore require (up to a phase factor)

$$\begin{aligned} \bar{b}_m(0) &= 1 \\ \bar{b}_s(0) &= 0 \qquad \text{if } s \neq m. \end{aligned} \tag{19.6}$$

Equivalently we can write

$$\bar{b}_s(0) = \delta_{ms} \tag{19.7}$$

Going in circles with a λ expansion In class it was hinted that we could try a λ expansion of the following form to determine a solution for the $\bar{b}_s$ coefficients at later times

$$\bar{b}_s(t) = \delta_{ms} + \lambda \bar{b}_s^{(1)}(t) + \cdots \tag{19.8}$$

I was not able to figure out how to make that work. Trying this first to first order, and plugging in, we find

$$\lambda \frac{d}{dt}\bar{b}_s^{(1)}(t) = -\sum_{n \neq s} (\delta_{mn} + \lambda \bar{b}_n^{(1)}(t)) e^{i\gamma_{sn}(t)} \left\langle \hat{\psi}_s(t) \right| \frac{d}{dt} \left|\hat{\psi}_n(t)\right\rangle, \tag{19.9}$$

equating powers of λ yields two equations

$$\begin{aligned} \frac{d}{dt}\bar{b}_s^{(1)}(t) &= -\sum_{n \neq s} \bar{b}_n^{(1)}(t) e^{i\gamma_{sn}(t)} \left\langle \hat{\psi}_s(t) \right| \frac{d}{dt} \left|\hat{\psi}_n(t)\right\rangle \\ 0 &= -\sum_{n \neq s} \delta_{mn} e^{i\gamma_{sn}(t)} \left\langle \hat{\psi}_s(t) \right| \frac{d}{dt} \left|\hat{\psi}_n(t)\right\rangle. \end{aligned} \tag{19.10}$$

Observe that the first identity is exactly what we started with in eq. (19.3), but has just replaced the $\bar{b}_n$'s with $\bar{b}_n^{(1)}$'s. Worse is that the second equation is only satisfied for $s = m$, and for $s \neq m$ we have

$$0 = -e^{i\gamma_{sm}(t)} \left\langle \hat{\psi}_s(t) \right| \frac{d}{dt} \left|\hat{\psi}_m(t)\right\rangle. \tag{19.11}$$

So this λ power series only appears to work if we somehow had $\left|\hat{\psi}_s(t)\right\rangle$ always orthonormal to the derivative of $\left|\hat{\psi}_m(t)\right\rangle$. Perhaps this could be done if the Hamiltonian was also expanded in powers of λ, but such a beastie seems foreign to the problem. Note that we do not even have any explicit dependence on the Hamiltonian in the final $\bar{b}_n$ differential equations, as we would probably need for such an expansion to work out.

A Taylor series expansion in time What we can do is to expand the $\bar{b}_n$'s in a power series parametrized by time. That is, again, assuming we started with energy equal to $\hbar\omega_m$, form

$$\bar{b}_s(t) = \delta_{sm} + \frac{t}{1!}\left(\frac{d}{dt}\bar{b}_s(t)\Big|_{t=0}\right) + \frac{t^2}{2!}\left(\frac{d^2}{dt^2}\bar{b}_s(t)\Big|_{t=0}\right) + \cdots \tag{19.12}$$

The first order term we can grab right from eq. (19.3) and find

$$\begin{aligned}
\frac{d\bar{b}_s(t)}{dt}\Big|_{t=0} &= -\sum_{n\neq s} \bar{b}_n(0)\left\langle\hat{\psi}_s(t)\right| \frac{d}{dt}\left|\hat{\psi}_n(t)\right\rangle\Big|_{t=0} \\
&= -\sum_{n\neq s} \delta_{nm}\left\langle\hat{\psi}_s(t)\right| \frac{d}{dt}\left|\hat{\psi}_n(t)\right\rangle\Big|_{t=0} \\
&= \begin{cases} 0 & s = m \\ -\left\langle\hat{\psi}_s(t)\right| \frac{d}{dt}\left|\hat{\psi}_m(t)\right\rangle\Big|_{t=0} & \\ & s \neq m \end{cases}
\end{aligned} \tag{19.13}$$

Let us write

$$\begin{aligned}
|n\rangle &= \left|\hat{\psi}_n(0)\right\rangle \\
\left|n'\right\rangle &= \frac{d}{dt}\left|\hat{\psi}_n(t)\right\rangle\Big|_{t=0}
\end{aligned} \tag{19.14}$$

So we can write

$$\frac{d\bar{b}_s(t)}{dt}\Big|_{t=0} = -(1-\delta_{sm})\left\langle s\middle|m'\right\rangle, \tag{19.15}$$

and form, to first order in time our approximation for the coefficient is

$$\bar{b}_s(t) = \delta_{sm} - t(1-\delta_{sm})\left\langle s\middle|m'\right\rangle. \tag{19.16}$$

Let us do the second order term too. For that we have

$$\frac{d^2}{dt^2}\bar{b}_s(t)\Big|_{t=0} = -\sum_{n\neq s}\left(\left(\frac{d}{dt}\bar{b}_n(t) + \delta_{nm}i\frac{d\gamma_{sn}(t)}{dt}\right)\langle s|n'\rangle + \delta_{nm}\frac{d}{dt}\left(\langle\hat{\psi}_s(t)|\,\frac{d}{dt}\,|\hat{\psi}_n(t)\rangle\right)\right)\Big|_{t=0} \tag{19.17}$$

For the γ_{sn} derivative we note that

$$\frac{d}{dt}\gamma_s(t)\Big|_{t=0} = \omega_s(0) - i\langle s|s'\rangle\,, \tag{19.18}$$

So we have

$$\frac{d^2}{dt^2}\bar{b}_s(t)\Big|_{t=0} = -\sum_{n\neq s}(-(1-\delta_{nm})\langle n|m'\rangle + \delta_{nm}i(\omega_{sn}(0) - i\langle s|s'\rangle + i\langle n|n'\rangle))\langle s|n'\rangle + \delta_{nm}(\langle s'|n'\rangle + \langle s|n''\rangle) \tag{19.19}$$

Again for $s = m$, all terms are killed. That is somewhat surprising, but suggests that we will need to normalize the coefficients after the perturbation calculation, since we have unity for one of them.

For $s \neq m$ we have

$$\begin{aligned}\frac{d^2}{dt^2}\bar{b}_s(t)\Big|_{t=0} &= \sum_{n\neq s}(\langle n|m'\rangle - \delta_{nm}i(\omega_{sn}(0) - i\langle s|s'\rangle + i\langle n|n'\rangle))\langle s|n'\rangle - \delta_{nm}(\langle s'|n'\rangle + \langle s|n''\rangle) \\ &= -i(\omega_{sm}(0) - i\langle s|s'\rangle + i\langle m|m'\rangle)\langle s|m'\rangle - (\langle s'|m'\rangle + \langle s|m''\rangle) + \sum_{n\neq s}\langle n|m'\rangle\langle s|n'\rangle\,.\end{aligned} \tag{19.20}$$

So we have, for $s \neq m$

$$\frac{d^2}{dt^2}\bar{b}_s(t)\Big|_{t=0} = (\langle m|m'\rangle - \langle s|s'\rangle)\langle s|m'\rangle - i\omega_{sm}(0)\langle s|m'\rangle - \langle s'|m'\rangle - \langle s|m''\rangle + \sum_{n\neq s}\langle n|m'\rangle\langle s|n'\rangle\,. \tag{19.21}$$

It is not particularly illuminating looking, but possible to compute, and we can use it to form a second order approximate solution for our perturbed state.

$$\begin{aligned}\bar{b}_s(t) &= \delta_{sm} - t(1-\delta_{sm})\langle s|m'\rangle \\ &\quad + (1-\delta_{sm})\left((\langle m|m'\rangle - \langle s|s'\rangle)\langle s|m'\rangle - i\omega_{sm}(0)\langle s|m'\rangle - \langle s'|m'\rangle - \langle s|m''\rangle + \sum_{n\neq s}\langle n|m'\rangle\langle s|n'\rangle\right)\frac{t^2}{2}\end{aligned}$$

(19.22)

New info. How to do the λ expansion Asking about this, Federico nicely explained. "The reason why you are going in circles when trying the lambda expansion is because you are not assuming the term $\langle\psi(t)|\,(d/dt)\,|\psi(t)\rangle$ to be of order lambda. This has to be assumed, otherwise it does not make sense at all trying a perturbative approach. This assumption means that the coupling between the level s and the other levels is assumed to be small because the time dependent part of the Hamiltonian is small or changes slowly with time. Making a Taylor expansion in time would be sensible only if you are interested in a short interval of time. The lambda-expansion approach would work for any time as long as the time dependent piece of the Hamiltonian does not change wildly or is too big."

In the tutorial he outlined another way to justify this. We have written so far

$$H = \begin{cases} H(t) & t > 0 \\ H_0 & t < 0 \end{cases} \tag{19.23}$$

where $H(0) = H_0$. We can make this explicit, and introduce a λ factor into the picture if we write

$$H(t) = H_0 + \lambda H'(t), \tag{19.24}$$

where H_0 has no time dependence, so that our Hamiltonian is then just the "steady-state" system for $\lambda = 0$.

Now recall the method from [2] that we can use to relate our bra-derivative-ket to the Hamiltonian. Taking derivatives of the energy identity, braketed between two independent kets ($m \neq n$) we have

$$\begin{aligned} 0 &= \left\langle \hat{\psi}_m(t) \right| \frac{d}{dt} \left(H(t) \left| \hat{\psi}_n(t) \right\rangle - \hbar\omega_n \left| \hat{\psi}_n(t) \right\rangle \right) \\ &= \left\langle \hat{\psi}_m(t) \right| \left(\frac{dH(t)}{dt} \left| \hat{\psi}_n(t) \right\rangle + H(t) \frac{d}{dt} \left| \hat{\psi}_n(t) \right\rangle - \hbar \frac{d\omega_n}{dt} \left| \hat{\psi}_n(t) \right\rangle - \hbar\omega_n \frac{d}{dt} \left| \hat{\psi}_n(t) \right\rangle \right) \\ &= \hbar(\omega_m - \omega_n) \left\langle \hat{\psi}_m(t) \right| \frac{d}{dt} \left| \hat{\psi}_n(t) \right\rangle - \cancel{\hbar \frac{d\omega_n}{dt} \delta_{mn}} + \left\langle \hat{\psi}_m(t) \right| \frac{dH(t)}{dt} \left| \hat{\psi}_n(t) \right\rangle \end{aligned} \tag{19.25}$$

So for $m \neq n$ we find a dependence between the bra-derivative-ket and the time derivative of the Hamiltonian

$$\left\langle \hat{\psi}_m(t) \right| \frac{d}{dt} \left| \hat{\psi}_n(t) \right\rangle = \frac{\left\langle \hat{\psi}_m(t) \right| \frac{dH(t)}{dt} \left| \hat{\psi}_n(t) \right\rangle}{\hbar(\omega_n - \omega_m)} \tag{19.26}$$

Referring back to eq. (19.24) we see the λ dependence in this quantity, coming directly from the λ dependence imposed on the time dependent part of the Hamiltonian

$$\left\langle \hat{\psi}_m(t) \right| \frac{d}{dt} \left| \hat{\psi}_n(t) \right\rangle = \lambda \frac{\left\langle \hat{\psi}_m(t) \right| \frac{dH'(t)}{dt} \left| \hat{\psi}_n(t) \right\rangle}{\hbar(\omega_n - \omega_m)} \tag{19.27}$$

Given this λ dependence, let us revisit the perturbation attempt of eq. (19.9). Our first order factors of λ are now

$$\begin{aligned} \frac{d}{dt} \bar{b}_s^{(1)}(t) &= -\sum_{n \neq s} \delta_{mn} e^{i\gamma_{sn}(t)} \left\langle \hat{\psi}_s(t) \right| \frac{d}{dt} \left| \hat{\psi}_n(t) \right\rangle \\ &= \begin{cases} 0 & \text{if } m = s \\ -e^{i\gamma_{sm}(t)} \left\langle \hat{\psi}_s(t) \right| \frac{d}{dt} \left| \hat{\psi}_m(t) \right\rangle & \text{if } m \neq s \end{cases} \end{aligned} \tag{19.28}$$

So we find to first order

$$\bar{b}_s(t) = \delta_{ms}(1 + \lambda \text{constant}) - (1 - \delta_{ms})\lambda \int_0^t dt' e^{i\gamma_{sm}(t')} \left\langle \hat{\psi}_s(t') \right| \frac{d}{dt'} \left| \hat{\psi}_m(t') \right\rangle \tag{19.29}$$

A couple observations of this result. One is that the constant factor in the $m = s$ case makes sense. This would likely be a negative contribution since we have to decrease the probability coefficient for finding our wavefunction in the $m = s$ state after perturbation, since we are increasing the probability for finding it elsewhere by changing the Hamiltonian.

Also observe that since $e^{i\gamma_{sm}} \sim 0$ for small t this is consistent with the first order Taylor series expansion where we found our first order contribution was

$$-(1 - \delta_{ms})t \left\langle \hat{\psi}_s(t) \right| \frac{d}{dt} \left| \hat{\psi}_m(t) \right\rangle. \tag{19.30}$$

Also note that this $-e^{i\gamma_{sm}(t')} \left\langle \hat{\psi}_s(t') \right| \frac{d}{dt'} \left| \hat{\psi}_m(t') \right\rangle$ is exactly the difference from 0 that was mentioned in class when the trial solution of $\bar{b}_s = \delta_{sm}$ was tested by plugging it into eq. (19.3), so it is not too surprising that we should have a factor of exactly this form when we refine our approximation.

A question to consider should we wish to refine the λ perturbation to higher than first order in λ: is there any sort of λ dependence in the $e^{i\gamma_{sm}}$ coming from the Γ_{sm} term in that exponential?

20

DEGENERACY AND DIAGONALIZATION

20.1 MOTIVATION

In class it was mentioned that to deal with perturbation around a degenerate energy eigenvalue, we needed to diagonalize the perturbing Hamiltonian. I did not follow those arguments completely, and I had like to revisit those here.

20.2 A FOUR STATE HAMILTONIAN

Problem set 3, problem 1, was to calculate the energy eigenvalues for the following Hamiltonian

$$\begin{aligned} H &= H_0 + \lambda H' \\ H_0 &= \begin{bmatrix} a & 0 & 0 & 0 \\ 0 & b & 0 & 0 \\ 0 & 0 & c & 0 \\ 0 & 0 & 0 & c \end{bmatrix} \\ H' &= \begin{bmatrix} \alpha & 0 & \nu & \eta \\ 0 & \beta & 0 & \mu \\ \nu^* & 0 & \gamma & 0 \\ \eta^* & \mu^* & 0 & \delta \end{bmatrix} \end{aligned} \tag{20.1}$$

This is more complicated that the two state problem that are solved exactly in §13.1.1 in the text [4], but differs from the (possibly) infinite dimensional problem that was covered in class. Unfortunately, the solution provided to this problem did not provide the illumination I expected, so let us do it again, calculating the perturbed energy eigenvalues for the degenerate levels, from scratch.

Can we follow the approach used in the text for the two (only) state problem. For the two state problem, it was assumed that the perturbed solution could be expressed as a superposition of the two states that formed the basis for the unperturbed Hilbert space. That is

$$|\psi\rangle = m\,|1\rangle + n\,|2\rangle \tag{20.2}$$

For the two state problem, assuming that the perturbed energy eigenvalue is E, and the unperturbed energy eigenvalue is E^0 we find

$$\begin{aligned} 0 &= (H - E)|\psi\rangle \\ &= (H_0 + \lambda H')|\psi\rangle - E|\psi\rangle \\ &= (H_0 + \lambda H')(m|1\rangle + n|2\rangle) - E(m|1\rangle + n|2\rangle) \\ &= \lambda H'(m|1\rangle + n|2\rangle) - E^0(m|1\rangle + n|2\rangle) \\ &= (-E^0 + \lambda H')\begin{bmatrix}|1\rangle & |2\rangle\end{bmatrix}\begin{bmatrix}m \\ n\end{bmatrix} \end{aligned} \tag{20.3}$$

Left multiplying by the brakets we find

$$\begin{aligned} 0 &= \begin{bmatrix}\langle 1| \\ \langle 2|\end{bmatrix}(H - E)|\psi\rangle \\ &= \left((E^0 - E)I + \lambda\begin{bmatrix}\langle 1|H'|1\rangle & \langle 1|H'|2\rangle \\ \langle 2|H'|1\rangle & \langle 2|H'|2\rangle\end{bmatrix}\right)\begin{bmatrix}m \\ n\end{bmatrix} \end{aligned} \tag{20.4}$$

Or

$$\left((E^0 - E)I + \lambda\left[H'_{ij}\right]\right)\begin{bmatrix}m \\ n\end{bmatrix} = 0. \tag{20.5}$$

Observe that there was no assumption about the dimensionality of H_0 and H' here, just that the two degenerate energy levels had eigenvalues E^0 and a pair of eigenkets $|1\rangle$ and $|2\rangle$ such that $H_0|i\rangle = E^0|i\rangle, i \in [1, 2]$. It is clear that we can use a similar argument for any degeneracy degree. It is also clear how to proceed, since we have what almost amounts to a characteristic equation for the degenerate subspace of Hilbert space for the problem.

Because H' is Hermitian, a diagonalization

$$\begin{aligned} H' &= U^* D U \\ D &= \left[\mathcal{H}'_i \delta_{ij}\right] \end{aligned} \tag{20.6}$$

can be found. To solve for E we can take the determinant of the matrix factor of eq. (20.5), and because $I = U^* U$ we have

$$\begin{aligned} 0 &= \left|(E^0 - E)U^* I U + \lambda U^* D U\right| \\ &= \left|U^*\right|\left|(E^0 - E)I + \lambda D\right|\left|U\right| \\ &= \begin{vmatrix} E^0 - E + \lambda \mathcal{H}'_1 & 0 \\ 0 & E^0 - E + \lambda \mathcal{H}'_2 \end{vmatrix} \\ &= (E^0 - E + \lambda \mathcal{H}'_1)(E^0 - E + \lambda \mathcal{H}'_2) \end{aligned} \tag{20.7}$$

So our energy eigenvalues associated with the perturbed state are (exactly)

$$E = E^0 + \lambda \mathcal{H}'_1, E^0 + \lambda \mathcal{H}'_2. \tag{20.8}$$

It is a bit curious seeming that only the energy eigenvalues associated with the degeneracy play any part in this result, but there is some intuitive comfort in this idea. Without the perturbation, we can not do an energy measurement that would distinguish one or the other of the eigenkets for the degenerate energy level, so it does not seem unreasonable that a perturbed energy level close to the original can be formed by superposition of these two states, and thus the perturbed energy eigenvalue for the new system would then be related to only those degenerate levels.

Observe that in the problem set three problem we had a diagonal initial Hamiltonian H_0, that does not have an impact on the argument above, since that portion of the Hamiltonian only has a diagonal contribution to the result found in eq. (20.5), since the identity $H_0 |i\rangle = c |i\rangle, i \in [3, 4]$ removes any requirement to know the specifics of that portion of the matrix element of H_0.

20.3 GENERALIZING SLIGHTLY

Let us work with a system that has kets using an explicit degeneracy index

$$H_0 |m\alpha_m\rangle = E^0_m |m\alpha_m\rangle, \qquad \alpha_m = 1, \cdots, \gamma_m, m \in [1, N] \tag{20.9}$$

Example:

$$\begin{aligned} |m\alpha_m\rangle \in & |11\rangle \\ & |21\rangle, |22\rangle \\ & |31\rangle \\ & |41\rangle, |42\rangle, |43\rangle. \end{aligned} \tag{20.10}$$

Again we seek to find the energy eigenvalues of the new system

$$H = H_0 + \lambda H'. \tag{20.11}$$

For any m with associated with a degeneracy ($\gamma_m > 1$) we can calculate the subspace diagonalization

$$\left[\langle mi| H' |mj\rangle\right] = U_m D_m U_m^\dagger, \tag{20.12}$$

where

$$U_m U_m^\dagger = 1, \tag{20.13}$$

and D_m is diagonal

$$D_m = \left[\delta_{ij}\mathcal{H}'_{m,i}\right]. \tag{20.14}$$

This is not a diagonalizing transformation in the usual sense. Putting it together into block matrix form, we can write

$$U = \begin{bmatrix} U_1 & & & \\ & U_2 & & \\ & & \ddots & \\ & & & U_N \end{bmatrix} \tag{20.15}$$

and find that a similarity transformation using this change of basis matrix puts all the block matrices along the diagonal into diagonal form, but leaves the rest possibly non-zero

$$U^\dagger \left[\left\langle m\alpha_{m_i}\right| H' |mj\rangle \left|m\alpha_{m_j}\right\rangle\right] U = \begin{bmatrix} D_1 & x & x & x \\ x & D_2 & x & x \\ x & x & \ddots & x \\ x & x & x & D_N \end{bmatrix} \tag{20.16}$$

A five level system with two pairs of degenerate levels Let us do this explicitly using a specific degeneracy example, supposing that we have a non-degenerate ground state, and two pairs doubly degenerate next energy levels. That is

$$\begin{aligned} |m\alpha_m\rangle \in & |11\rangle \\ & |21\rangle, |22\rangle \\ & |31\rangle, |32\rangle \end{aligned} \tag{20.17}$$

Our change of basis matrix is

$$U = \left[\begin{array}{c|cc|cc} 1 & 0 & 0 & 0 & 0 \\ \hline 0 & \multicolumn{2}{c|}{\multirow{2}{*}{U_2}} & 0 & 0 \\ 0 & & & 0 & 0 \\ \hline 0 & 0 & 0 & \multicolumn{2}{c}{\multirow{2}{*}{U_3}} \\ 0 & 0 & 0 & & \end{array}\right] \tag{20.18}$$

We would like to calculate

$$U^\dagger H' U \tag{20.19}$$

Let us write this putting row and column range subscripts on our matrices to explicitly block them into multiplication compatible sized pieces

$$\begin{aligned} U &= \begin{bmatrix} I_{11,11} & 0_{11,23} & 0_{11,45} \\ 0_{23,11} & U_{23,23} & 0_{23,45} \\ 0_{45,11} & 0_{45,23} & U_{45,45} \end{bmatrix} \\ H' &= \begin{bmatrix} H'_{11,11} & H'_{11,23} & H'_{11,45} \\ H'_{23,11} & H'_{23,23} & H'_{23,45} \\ H'_{45,11} & H'_{45,23} & H'_{45,45} \end{bmatrix} \end{aligned} \tag{20.20}$$

The change of basis calculation then becomes

$$
\begin{aligned}
U^\dagger H' U &= \begin{bmatrix} I_{11,11} & 0_{11,23} & 0_{11,45} \\ 0_{23,11} & U^\dagger_{23,23} & 0_{23,45} \\ 0_{45,11} & 0_{45,23} & U^\dagger_{45,45} \end{bmatrix} \begin{bmatrix} H'_{11,11} & H'_{11,23} & H'_{11,45} \\ H'_{23,11} & H'_{23,23} & H'_{23,45} \\ H'_{45,11} & H'_{45,23} & H'_{45,45} \end{bmatrix} \begin{bmatrix} I_{11,11} & 0_{11,23} & 0_{11,45} \\ 0_{23,11} & U_{23,23} & 0_{23,45} \\ 0_{45,11} & 0_{45,23} & U_{45,45} \end{bmatrix} \\
&= \begin{bmatrix} I_{11,11} & 0_{11,23} & 0_{11,45} \\ 0_{23,11} & U^\dagger_{23,23} & 0_{23,45} \\ 0_{45,11} & 0_{45,23} & U^\dagger_{45,45} \end{bmatrix} \begin{bmatrix} H'_{11,11} & H'_{11,23}U_{23,23} & H'_{11,45}U_{45,45} \\ H'_{23,11} & H'_{23,23}U_{23,23} & H'_{23,45}U_{45,45} \\ H'_{45,11} & H'_{45,23}U_{23,23} & H'_{45,45}U_{45,45} \end{bmatrix} \\
&= \begin{bmatrix} H'_{11,11} & H'_{11,23}U_{23,23} & H'_{11,45}U_{45,45} \\ U^\dagger_{23,23}H'_{23,11} & U^\dagger_{23,23}H'_{23,23}U_{23,23} & U^\dagger_{23,23}H'_{23,45}U_{45,45} \\ U^\dagger_{45,45}H'_{45,11} & U^\dagger_{45,45}H'_{45,23}U_{23,23} & U^\dagger_{45,45}H'_{45,45}U_{45,45} \end{bmatrix}
\end{aligned}
\tag{20.21}
$$

We see that we end up with explicitly diagonal matrices along the diagonal blocks, but products that are otherwise everywhere else.

In the new basis our kets become

$$
\left|m\alpha'_m\right\rangle = U^\dagger \left|m\alpha_m\right\rangle \tag{20.22}
$$

Suppose we calculate this change of basis representation for $|21\rangle$ (we have implicitly assumed above that our original basis had the ordering $\{|11\rangle|21\rangle, |22\rangle, |31\rangle, |32\rangle\}$). We find

$$
\begin{aligned}
\left|21'\right\rangle &= U^* |21\rangle \\
&= \begin{bmatrix} 1 & 0 & 0 \\ 0 & U^*_2 & 0 \\ 0 & 0 & U^*_3 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}
\end{aligned}
\tag{20.23}
$$

With

$$
\begin{aligned}
U_2 &= \begin{bmatrix} U_{2,11} & U_{2,12} \\ U_{2,21} & U_{2,22} \end{bmatrix} \\
U_2^\dagger &= \begin{bmatrix} U^*_{2,11} & U^*_{2,21} \\ U^*_{2,12} & U^*_{2,22} \end{bmatrix}
\end{aligned}
\tag{20.24}
$$

We find

$$\begin{aligned}\left|21'\right\rangle &= U^* \left|21'\right\rangle \\ &= \begin{bmatrix} 0 \\ U^*_{2,11} \\ U^*_{2,12} \\ 0 \\ 0 \end{bmatrix} \quad = U^*_{2,11} \left|21\right\rangle + U^*_{2,12} \left|22\right\rangle\end{aligned} \tag{20.25}$$

Energy eigenvalues of the unperturbed Hamiltonian in the new basis Generalizing this, it is clear that for a given degeneracy level, the transformed kets in the new basis are superposition of only the kets associated with that degenerate level (and the kets for the non-degenerate levels are left as is).

Even better, we have for all $\left|m\alpha'_m\right\rangle = U^\dagger \left|m\alpha_m\right\rangle$ that $\left|m\alpha'_m\right\rangle$ remain eigenkets of the unperturbed Hamiltonian. We see that by computing the matrix element of our Hamiltonian in the full basis.

Writing

$$F = U^\dagger H' U, \tag{20.26}$$

or

$$H' = UFU^\dagger, \tag{20.27}$$

where F has been shown to have diagonal block diagonals, we can write

$$\begin{aligned}H &= H_0 + \lambda UFU^\dagger \\ &= UU^\dagger H_0 UU^\dagger + \lambda UFU^\dagger \\ &= U(U^\dagger H_0 U + \lambda F)U^\dagger\end{aligned} \tag{20.28}$$

So in the $\left|m\alpha'_m\right\rangle$ basis, our Hamiltonian's matrix element is

$$H \to U^\dagger H_0 U + \lambda F \tag{20.29}$$

When $\lambda = 0$, application of this Hamiltonian to the new basis kets gives

$$\begin{aligned} H_0 \left|m\alpha'\right\rangle &= U^\dagger H_0 U U^\dagger \left|m\alpha\right\rangle \\ &= U^\dagger H_0 \left|m\alpha\right\rangle \\ &= U^\dagger \mathcal{H}_m^0 \left|m\alpha\right\rangle \\ &= \mathcal{H}_m^0 \left(U^\dagger \left|m\alpha\right\rangle\right) \end{aligned} \tag{20.30}$$

But this is just

$$H_0 \left|m\alpha'\right\rangle = \mathcal{H}_m^0 \left|m\alpha'\right\rangle, \tag{20.31}$$

a statement that the $|m\alpha'\rangle$ are still the energy eigenkets for the unperturbed system. This matches our expectations since we have seen that these differ from the original basis elements only for degenerate energy levels, and that these new basis elements are superpositions of only the kets for their respective degeneracy levels.

21

REVIEW OF APPROXIMATION RESULTS

21.1 MOTIVATION

Here I will summarize what I had put on a cheat sheet for the tests or exam, if one would be allowed. While I can derive these results, memorization unfortunately appears required for good test performance in this class, and this will give me a good reference of what to memorize.

This set of review notes covers all the approximation methods we covered except for Fermi's golden rule.

21.2 VARIATIONAL METHOD

We can find an estimate of our ground state energy using

$$\boxed{\frac{\langle\Psi|\, H\,|\Psi\rangle}{\langle\Psi|\Psi\rangle} \geq E_0} \tag{21.1}$$

21.3 TIME INDEPENDENT PERTURBATION

Given a perturbed Hamiltonian and an associated solution for the unperturbed state

$$\boxed{\begin{aligned} H &= H_0 + \lambda H', \qquad \lambda \in [0,1] \\ H_0 \left|{\psi_{m\alpha}}^{(0)}\right\rangle &= {E_m}^{(0)} \left|{\psi_{m\alpha}}^{(0)}\right\rangle, \end{aligned}} \tag{21.2}$$

we assume a power series solution for the energy

$$E_m = {E_m}^{(0)} + \lambda {E_m}^{(1)} + \lambda^2 {E_m}^{(2)} + \cdots \tag{21.3}$$

For a non-degenerate state $|\psi_m\rangle = |\psi_{m1}\rangle$, with an unperturbed value of $\left|\psi_m^{(0)}\right\rangle = \left|\psi_{m1}^{(0)}\right\rangle$, we seek a power series expansion of this ket in the perturbed system

$$\begin{aligned} |\psi_m\rangle &= \sum_{n,\alpha} {c_{n\alpha;m}}^{(0)} \left|{\psi_{n\alpha}}^{(0)}\right\rangle + \lambda \sum_{n,\alpha} {c_{n\alpha;m}}^{(1)} \left|{\psi_{n\alpha}}^{(0)}\right\rangle + \lambda^2 \sum_{n,\alpha} {c_{n\alpha;m}}^{(2)} \left|{\psi_{n\alpha}}^{(0)}\right\rangle + \cdots \\ &\propto \left|{\psi_m}^{(0)}\right\rangle + \lambda \sum_{n\neq m,\alpha} {\bar{c}_{n\alpha;m}}^{(1)} \left|{\psi_{n\alpha}}^{(0)}\right\rangle + \lambda^2 \sum_{n\neq m,\alpha} {\bar{c}_{n\alpha;m}}^{(2)} \left|{\psi_{n\alpha}}^{(0)}\right\rangle + \cdots \end{aligned} \tag{21.4}$$

Any states $n \neq m$ are allowed to have degeneracy. For this case, we found to second order in energy and first order in the kets

$$\begin{aligned} E_m &= E_m^{(0)} + \lambda {H_{m1;m1}}' + \lambda^2 \sum_{n\neq m,\alpha} \frac{\left|{H_{n\alpha;m1}}'\right|^2}{E_m^{(0)} - E_n^{(0)}} + \cdots \\ |\psi_m\rangle &\propto \left|{\psi_m}^{(0)}\right\rangle + \lambda \sum_{n\neq m,\alpha} \frac{{H_{n\alpha;m1}}'}{E_m^{(0)} - E_n^{(0)}} \left|{\psi_{n\alpha}}^{(0)}\right\rangle + \cdots \\ H'_{n\alpha;s\beta} &= \left\langle {\psi_{n\alpha}}^{(0)}\right| H' \left|{\psi_{s\beta}}^{(0)}\right\rangle. \end{aligned} \tag{21.5}$$

21.4 DEGENERACY

When the initial energy eigenvalue E_m has a degeneracy $\gamma_m > 1$ we use a different approach to compute the perturbed energy eigenkets and perturbed energy eigenvalues. Writing the kets as $|m\alpha\rangle$, then we assume that the perturbed ket is a superposition of the kets in the degenerate energy level

$$|m\alpha\rangle' = \sum_i c_i |mi\rangle. \tag{21.6}$$

We find that we must have

$$\left((E^0 - E)I + \lambda \left[H'_{mi;mj}\right]\right) \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_{\gamma_m} \end{bmatrix} = 0. \tag{21.7}$$

Diagonalizing this matrix $\left[H'_{mi;mj}\right]$ (a subset of the complete H' matrix element)

$$\left[\langle mi| H' |mj\rangle\right] = U_m \left[\delta_{ij} \mathcal{H}'_{m,i}\right] U_m^\dagger, \tag{21.8}$$

we find, by taking the determinant, that the perturbed energy eigenvalues are in the set

$$\boxed{E = E^0_m + \lambda \mathcal{H}'_{m,i}, \quad i \in [1, \gamma_m]} \tag{21.9}$$

To compute the perturbed kets we must work in a basis for which the block diagonal matrix elements are diagonal for all m, as in

$$\left[\langle mi| H' |mj\rangle\right] = \left[\delta_{ij}\mathcal{H}'_{m,i}\right]. \tag{21.10}$$

If that is not the case, then the unitary matrices of eq. (21.8) can be computed, and the matrix

$$U = \begin{bmatrix} U_1 & & & \\ & U_2 & & \\ & & \ddots & \\ & & & U_N \end{bmatrix}, \tag{21.11}$$

can be formed. The kets

$$|\overline{m\alpha}\rangle = U^\dagger |m\alpha\rangle\,, \tag{21.12}$$

will still be energy eigenkets of the unperturbed Hamiltonian

$$H_0 |\overline{m\alpha}\rangle = E^0_m |\overline{m\alpha}\rangle\,, \tag{21.13}$$

but also ensure that the partial diagonalization condition of eq. (21.8) is satisfied. In this basis, dropping overbars, the first order perturbation results found previously for perturbation about a non-degenerate state also hold, allowing us to write

$$\boxed{|s\alpha\rangle' = |s\alpha\rangle + \lambda \sum_{m\neq s,\beta} \frac{H'_{m\beta;s\alpha}}{E^{(0)}_s - E^{(0)}_m} |m\beta\rangle + \cdots} \tag{21.14}$$

21.5 INTERACTION PICTURE

We split of the Hamiltonian into time independent and time dependent parts, and also factorize the time evolution operator

$$\boxed{\begin{aligned} H &= H_0 + H_I(t) \\ |\alpha_S\rangle &= e^{-iH_0 t/\hbar}\,|\alpha_I(t)\rangle = e^{-iH_0 t/\hbar} U_I(t)\,|\alpha_I(0)\rangle\,. \end{aligned}} \tag{21.15}$$

Plugging into Schrödinger's equation we find

$$\boxed{\begin{aligned} i\hbar\frac{d}{dt}\,|\alpha_I(t)\rangle &= H_I(t)\,|\alpha_I(t)\rangle \\ i\hbar\frac{dU_I}{dt} &= H_I' U_I \\ H_I'(t) &= e^{iH_0 t/\hbar} H_I(t) e^{-iH_0 t/\hbar} \end{aligned}} \tag{21.16}$$

21.6 TIME DEPENDENT PERTURBATION

We moved on to time dependent perturbations of the form

$$\boxed{\begin{aligned} H(t) &= H_0 + H'(t) \\ H_0\left|\psi_n^{(0)}\right\rangle &= \hbar\omega_n\left|\psi_n^{(0)}\right\rangle. \end{aligned}} \tag{21.17}$$

where $\hbar\omega_n$ are the energy eigenvalues, and $\left|\psi_n^{(0)}\right\rangle$ the energy eigenstates of the unperturbed Hamiltonian.

Use of the interaction picture led quickly to the problem of seeking the coefficients describing the perturbed state

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-i\omega_n t}\left|\psi_n^{(0)}\right\rangle, \tag{21.18}$$

and plugging in we found

$$\boxed{\begin{aligned} i\hbar\dot{c}_s &= \sum_n H'_{sn}(t) e^{i\omega_{sn}t} c_n(t) \\ \omega_{sn} &= \omega_s - \omega_n \\ H'_{sn}(t) &= \left\langle\psi_s^{(0)}\right| H'(t)\left|\psi_n^{(0)}\right\rangle, \end{aligned}} \tag{21.19}$$

Perturbation expansion in series Introducing a λ parametrized dependence in the perturbation above, and assuming a power series expansion of our coefficients

$$\boxed{\begin{aligned} &H'(t) \to \lambda H'(t) \\ &c_s(t) = c_s^{(0)}(t) + \lambda c_s^{(1)}(t) + \lambda^2 c_s^{(2)}(t) + \cdots \end{aligned}} \tag{21.20}$$

we found, after equating powers of λ a set of coupled differential equations

$$\begin{aligned} i\hbar \dot{c}_s^{(0)}(t) &= 0 \\ i\hbar \dot{c}_s^{(1)}(t) &= \sum_n H'_{sn}(t) e^{i\omega_{sn}t} c_n^{(0)}(t) \\ i\hbar \dot{c}_s^{(2)}(t) &= \sum_n H'_{sn}(t) e^{i\omega_{sn}t} c_n^{(1)}(t) \\ &\vdots \end{aligned} \tag{21.21}$$

Of particular value was the expansion, assuming that we started with an initial state in energy level m before the perturbation was "turned on" (ie: $\lambda = 0$).

$$|\psi(t)\rangle = e^{-i\omega_m t} \left|\psi_m^{(0)}\right\rangle \tag{21.22}$$

So that $c_n^{(0)}(t) = \delta_{nm}$. We then found a first order approximation for the transition probability coefficient of

$$\boxed{i\hbar \dot{c}_m^{(1)} = H'_{ms}(t) e^{i\omega_{ms}t}} \tag{21.23}$$

21.7 SUDDEN PERTURBATIONS

The idea here is that we integrate Schrödinger's equation over the small interval containing the changing Hamiltonian

$$|\psi(t)\rangle = |\psi(t_0)\rangle + \frac{1}{i\hbar} \int_{t_0}^{t} H(t') \left|\psi(t')\right\rangle dt' \tag{21.24}$$

and find

$$\boxed{|\psi_{\text{after}}\rangle = |\psi_{\text{before}}\rangle\,.} \tag{21.25}$$

An implication is that, say, we start with a system measured in a given energy, that same system after the change to the Hamiltonian will then be in a state that is now a superposition of eigenkets from the new Hamiltonian.

21.8 ADIABATIC PERTURBATIONS

Given a Hamiltonian that turns on slowly at $t = 0$, a set of instantaneous eigenkets for the duration of the time dependent interval, and a representation in terms of the instantaneous eigenkets

$$\boxed{\begin{aligned} H(t) &= H_0, \qquad t \leq 0 \\ H(t)\left|\hat{\psi}_n(t)\right\rangle &= E_n(t)\left|\hat{\psi}_n(t)\right\rangle \\ |\psi\rangle &= \sum_n \bar{b}_n(t) e^{-i\alpha_n + i\beta_n}\left|\hat{\psi}_n\right\rangle \\ \alpha_n(t) &= \frac{1}{\hbar}\int_0^t dt' E_n(t'), \end{aligned}} \tag{21.26}$$

plugging into Schrödinger's equation we find

$$\boxed{\begin{aligned} \frac{d\bar{b}_m}{dt} &= -\sum_{n\neq m} \bar{b}_n e^{-i\gamma_{nm}} \left\langle \hat{\psi}_m(t)\right| \frac{d}{dt}\left|\hat{\psi}_n(t)\right\rangle \\ \gamma_{nm}(t) &= \alpha_n(t) - \alpha_m(t) - (\beta_n(t) - \beta_m(t)) \\ \beta_n(t) &= \int_0^t dt' \Gamma_n(t') \\ \Gamma_n(t) &= i\left\langle \hat{\psi}_n(t)\right| \frac{d}{dt}\left|\hat{\psi}_n(t)\right\rangle \end{aligned}} \tag{21.27}$$

Here $\Gamma_n(t)$ is called the Berry phase.

Evolution of a given state Given a system initially measured with energy $E_m(0)$ before the time dependence is "turned on"

$$\boxed{|\psi(0)\rangle = \left|\hat{\psi}_m(0)\right\rangle,} \tag{21.28}$$

we find that the first order Taylor series expansion for the transition probability coefficients are

$$\boxed{\bar{b}_s(t) = \delta_{sm} - t(1-\delta_{sm})\left\langle \hat{\psi}_s(0)\right| \frac{d}{dt}\left|\hat{\psi}_m(t)\right\rangle\Big|_{t=0}.} \tag{21.29}$$

If we introduce a λ perturbation, separating all the (slowly changing) time dependent part of the Hamiltonian H' from the non time dependent parts H_0 as in

$$H(t) = H_0 + \lambda H'(t) \tag{21.30}$$

then we find our perturbed coefficients are

$$\bar{b}_s(t) = \delta_{ms}(1 + \lambda\text{constant}) - (1 - \delta_{ms})\lambda \int_0^t dt' e^{i\gamma_{sm}(t')} \left\langle \hat{\psi}_s(t') \right| \frac{d}{dt'} \left| \hat{\psi}_m(t') \right\rangle \tag{21.31}$$

21.9 WKB

We write Schrödinger's equation as

$$\begin{aligned} 0 &= \frac{d^2U}{dx^2} + k^2 U \\ k^2 &= -\kappa^2 = \frac{2m(E-V)}{\hbar}. \end{aligned} \tag{21.32}$$

and seek solutions of the form $U \propto e^{i\phi}$. Schrödinger's equation takes the form

$$-(\phi'(x))^2 + i\phi''(x) + k^2(x) = 0. \tag{21.33}$$

Initially setting $\phi'' = 0$ we refine our approximation to find

$$\phi'(x) = k(x)\sqrt{1 + i\frac{k'(x)}{k^2(x)}}. \tag{21.34}$$

To first order, this gives us

$$U(x) \propto \frac{1}{\sqrt{k(x)}} e^{\pm i \int dx k(x)} \tag{21.35}$$

What we did not cover in class, but required in the problems was the Bohr-Sommerfeld condition described in §24.1.2 of the text [4].

$$\int_{x_1}^{x_2} dx \sqrt{2m(E - V(x))} = \left(n + \frac{1}{2}\right)\pi\hbar. \tag{21.36}$$

This was found from the WKB connection formulas, themselves found my some Bessel function arguments that I have to admit that I did not understand.

22

ON CONDITIONS FOR CLEBSH-GORDAN COEFFICIENTS TO BE ZERO

22.1 MOTIVATION

In §28.2 of the text [4] is a statement that the Clebsh-Gordan coefficient

$$\langle m_1 m_2 | jm \rangle \tag{22.1}$$

unless $m = m_1 + m_2$. It appeared that it was related to the operation of J_z, but how exactly was not obvious to me. In tutorial today we hashed through this. Here is the details lying behind this statement

22.2 RECAP ON NOTATION

We are taking an arbitrary two particle ket and decomposing it utilizing an insertion of a complete set of states

$$|jm\rangle = \sum_{m_1' m_2'} \left(\left| j_1 m_1' \right\rangle \left| j_2 m_2' \right\rangle \left\langle j_1 m_1' \right| \left\langle j_2 m_2' \right| \right) |jm\rangle \tag{22.2}$$

with j_1 and j_2 fixed, this is written with the shorthand

$$\begin{aligned} |j_1 m_1\rangle |j_2 m_2\rangle &= |m_1 m_2\rangle \\ \langle j_1 m_1 | \langle j_2 m_2 | |jm\rangle &= \langle m_1 m_2 | jm \rangle , \end{aligned} \tag{22.3}$$

so that we write

$$|jm\rangle = \sum_{m_1' m_2'} \left| m_1' m_2' \right\rangle \left\langle m_1' m_2' | jm \right\rangle \tag{22.4}$$

22.3 THE J_z ACTION

We have two ways that we can apply the operator J_z to $|jm\rangle$. One is using the sum above, for which we find

$$\begin{aligned} J_z|jm\rangle &= \sum_{m_1' m_2'} J_z \left|m_1' m_2'\right\rangle \left\langle m_1' m_2' \middle| jm\right\rangle \\ &= \hbar \sum_{m_1' m_2'} (m_1' + m_2') \left|m_1' m_2'\right\rangle \left\langle m_1' m_2' \middle| jm\right\rangle \end{aligned} \tag{22.5}$$

We can also act directly on $|jm\rangle$ and then insert a complete set of states

$$\begin{aligned} J_z|jm\rangle &= \sum_{m_1' m_2'} \left|m_1' m_2'\right\rangle \left\langle m_1' m_2' \middle| J_z|jm\right\rangle \\ &= \hbar m \sum_{m_1' m_2'} \left|m_1' m_2'\right\rangle \left\langle m_1' m_2' \middle| jm\right\rangle \end{aligned} \tag{22.6}$$

This provides us with the identity

$$m \sum_{m_1' m_2'} \left|m_1' m_2'\right\rangle \left\langle m_1' m_2' \middle| jm\right\rangle = \sum_{m_1' m_2'} (m_1' + m_2') \left|m_1' m_2'\right\rangle \left\langle m_1' m_2' \middle| jm\right\rangle \tag{22.7}$$

This equality must be valid for any $|jm\rangle$, and since all the kets $\left|m_1' m_2'\right\rangle$ are linearly independent, we must have for any m_1', m_2'

$$(m - m_1' - m_2') \left\langle m_1' m_2' \middle| jm\right\rangle \left|m_1' m_2'\right\rangle = 0 \tag{22.8}$$

We have two ways to get this zero. One of them is a $m = m_1' + m_2'$ condition, and the other is for the CG coeff $\left\langle m_1' m_2' \middle| jm\right\rangle$ to be zero whenever $m \neq m_1' + m_2'$.

It is not a difficult argument, but one that was not clear from a read of the text (at least to me).

23

ONE MORE ADIABATIC PERTURBATION DERIVATION

23.1 MOTIVATION

I liked one of the adiabatic perturbation derivations that I did to review the material, and am recording it for reference.

23.2 BUILD UP

In time dependent perturbation we started after noting that our ket in the interaction picture, for a Hamiltonian $H = H_0 + H'(t)$, took the form

$$|\alpha_S(t)\rangle = e^{-iH_0 t/\hbar} |\alpha_I(t)\rangle = e^{-iH_0 t/\hbar} U_I(t) |\alpha_I(0)\rangle . \tag{23.1}$$

Here we have basically assumed that the time evolution can be factored into a portion dependent on only the static portion of the Hamiltonian, with some other operator $U_I(t)$, providing the remainder of the time evolution. From eq. (23.1) that operator $U_I(t)$ is found to behave according to

$$i\hbar \frac{dU_I}{dt} = e^{iH_0 t/\hbar} H'(t) e^{-iH_0 t/\hbar} U_I, \tag{23.2}$$

but for our purposes we just assumed it existed, and used this for motivation. With the assumption that the interaction picture kets can be written in terms of the basis kets for the system at $t = 0$ we write our Schrödinger ket as

$$|\psi\rangle = \sum_k e^{-iH_0 t/\hbar} a_k(t) |k\rangle = \sum_k e^{-i\omega_k t/\hbar} a_k(t) |k\rangle , \tag{23.3}$$

where $|k\rangle$ are the energy eigenkets for the initial time equation problem

$$H_0 |k\rangle = E_k^0 |k\rangle . \tag{23.4}$$

23.3 ADIABATIC CASE

For the adiabatic problem, we assume the system is changing very slowly, as described by the instantaneous energy eigenkets

$$H(t)\,|k(t)\rangle = E_k(t)\,|k(t)\rangle\,. \tag{23.5}$$

Can we assume a similar representation to eq. (23.3) above, but allow $|k\rangle$ to vary in time? This does not quite work since $|k(t)\rangle$ are no longer eigenkets of H_0

$$|\psi\rangle = \sum_k e^{-iH_0 t/\hbar} a_k(t)\,|k(t)\rangle \neq \sum_k e^{-i\omega_k t} a_k(t)\,|k(t)\rangle\,. \tag{23.6}$$

Operating with $e^{iH_0 t/\hbar}$ does not give the proper time evolution of $|k(t)\rangle$, and we will in general have a more complex functional dependence in our evolution operator for each $|k(t)\rangle$. Instead of an $\omega_k t$ dependence in this time evolution operator let us assume we have some function $\alpha_k(t)$ to be determined, and can write our ket as

$$|\psi\rangle = \sum_k e^{-i\alpha_k(t)} a_k(t)\,|k(t)\rangle\,. \tag{23.7}$$

Operating on this with our energy operator equation we have

$$\begin{aligned} 0 &= \left(H - i\hbar\frac{d}{dt}\right)|\psi\rangle \\ &= \left(H - i\hbar\frac{d}{dt}\right)\sum_k e^{-i\alpha_k} a_k\,|k\rangle \\ &= \sum_k e^{-i\alpha_k(t)}\left((E_k a_k - i\hbar(-i\alpha_k' a_k + a_k'))\,|k\rangle - i\hbar a_k\left|k'\right\rangle\right) \end{aligned} \tag{23.8}$$

Here I have written $|k'\rangle = d\,|k\rangle\,/dt$. In our original time dependent perturbation the $-i\alpha_k'$ term was $-i\omega_k$, so this killed off the E_k. If we assume this still kills off the E_k, we must have

$$\alpha_k = \frac{1}{\hbar}\int_0^t E_k(t')dt', \tag{23.9}$$

and are left with

$$0 = \sum_k e^{-i\alpha_k(t)}\left(a_k'\,|k\rangle + a_k\left|k'\right\rangle\right). \tag{23.10}$$

Bra'ing with $\langle m|$ we have

$$0 = e^{-i\alpha_m(t)}a_m' + e^{-i\alpha_m(t)}a_m \langle m\big|m'\rangle + \sum_{k\neq m} e^{-i\alpha_k(t)}a_k \langle m\big|k'\rangle\,, \tag{23.11}$$

or

$$a_m' + a_m \langle m\big|m'\rangle = -\sum_{k\neq m} e^{-i\alpha_k(t)}e^{i\alpha_m(t)}a_k \langle m\big|k'\rangle\,, \tag{23.12}$$

The LHS is a perfect differential if we introduce an integration factor $e^{\int_0^t\langle m|m'\rangle}$, so we can write

$$e^{-\int_0^t\langle m|m'\rangle}(a_m e^{\int_0^t\langle m|m'\rangle})' = -\sum_{k\neq m} e^{-i\alpha_k(t)}e^{i\alpha_m(t)}a_k \langle m\big|k'\rangle\,, \tag{23.13}$$

This suggests that we want to form a new function

$$b_m = a_m e^{\int_0^t\langle m|m'\rangle} \tag{23.14}$$

or

$$a_m = b_m e^{-\int_0^t\langle m|m'\rangle} \tag{23.15}$$

Plugging this into our assumed representation we have a more concrete form

$$|\psi\rangle = \sum_k e^{-\int_0^t dt'(i\omega_k + \langle k|k'\rangle)}b_k(t)\,|k(t)\rangle\,. \tag{23.16}$$

Writing

$$\Gamma_k = i\langle k\big|k'\rangle\,, \tag{23.17}$$

this becomes

$$|\psi\rangle = \sum_k e^{-i\int_0^t dt'(\omega_k - \Gamma_k)}b_k(t)\,|k(t)\rangle\,. \tag{23.18}$$

A final pass Now that we have what appears to be a good representation for any given state if we wish to examine the time evolution, let us start over, reapplying our instantaneous energy operator equality

$$\begin{aligned} 0 &= \left(H - i\hbar\frac{d}{dt}\right)|\psi\rangle \\ &= \left(H - i\hbar\frac{d}{dt}\right)\sum_k e^{-i\int_0^t dt'(\omega_k - \Gamma_k)} b_k |k\rangle \\ &= -i\hbar\sum_k e^{-i\int_0^t dt'(\omega_k - \Gamma_k)}\left(i\Gamma_k b_k |k\rangle + b_k' |k\rangle + b_k \left|k'\right\rangle\right). \end{aligned} \tag{23.19}$$

Bra'ing with $\langle m|$ we find

$$\begin{aligned} 0 &= e^{-i\int_0^t dt'(\omega_m - \Gamma_m)} i\Gamma_m b_m + e^{-i\int_0^t dt'(\omega_m - \Gamma_m)} b_m' \\ &+ e^{-i\int_0^t dt'(\omega_m - \Gamma_m)} b_m \langle m\left|m'\right\rangle + \sum_{k\neq m} e^{-i\int_0^t dt'(\omega_k - \Gamma_k)} b_k \langle m\left|k'\right\rangle \end{aligned} \tag{23.20}$$

Since $i\Gamma_m = \langle m|m'\rangle$ the first and third terms cancel leaving us just

$$b_m' = -\sum_{k\neq m} e^{-i\int_0^t dt'(\omega_{km} - \Gamma_{km})} b_k \langle m\left|k'\right\rangle, \tag{23.21}$$

where $\omega_{km} = \omega_k - \omega_m$ and $\Gamma_{km} = \Gamma_k - \Gamma_m$.

23.4 SUMMARY

We assumed that a ket for the system has a representation in the form

$$|\psi\rangle = \sum_k e^{-i\alpha_k(t)} a_k(t) |k(t)\rangle, \tag{23.22}$$

where $a_k(t)$ and $\alpha_k(t)$ are given or to be determined. Application of our energy operator identity provides us with an alternate representation that simplifies the results

$$|\psi\rangle = \sum_k e^{-i\int_0^t dt'(\omega_k - \Gamma_k)} b_k(t) |k(t)\rangle. \tag{23.23}$$

With

$$\begin{aligned} \left|m'\right\rangle &= \frac{d}{dt}\left|m\right\rangle \\ \Gamma_k &= i\left\langle m\middle|m'\right\rangle \\ \omega_{km} &= \omega_k - \omega_m \\ \Gamma_{km} &= \Gamma_k - \Gamma_m \end{aligned} \tag{23.24}$$

we find that our dynamics of the coefficients are related by

$$b'_m = -\sum_{k\neq m} e^{-i\int_0^t dt'(\omega_{km}-\Gamma_{km})} b_k \left\langle m\middle|k'\right\rangle, \tag{23.25}$$

24

A SUPER SHORT DERIVATION OF THE TIME DEPENDENT PERTURBATION RESULT

With

$$|\psi t\rangle = \sum_k c_k(t) e^{-i\omega_k t} |k\rangle \tag{24.1}$$

apply the energy eigenvalue operator identity

$$\begin{aligned} 0 &= \left(H_0 + H' - i\hbar \frac{d}{dt}\right) |\psi t\rangle \\ &= \left(H_0 + H' - i\hbar \frac{d}{dt}\right) \sum_k c_k e^{-i\omega_k t} |k\rangle \\ &= \sum_k e^{-i\omega_k t} \left(\cancel{c_k E_k} + H' c_k - \cancel{i\hbar(-i\omega_k) c_k} - i\hbar c_k'\right) |k\rangle \end{aligned} \tag{24.2}$$

Bra with $\langle m|$

$$\sum_k e^{-i\omega_k t} H'_{mk} c_k = i\hbar e^{-i\omega_m t} c_m', \tag{24.3}$$

or

$$c_m' = \frac{1}{i\hbar} \sum_k e^{-i\omega_{km} t} H'_{mk} c_k \tag{24.4}$$

Now we can make the assumptions about the initial state and away we go.

25

SECOND FORM OF ADIABATIC APPROXIMATION

Motivation In class we were shown an adiabatic approximation where we started with (or worked our way towards) a representation of the form

$$|\psi\rangle = \sum_k c_k(t) e^{-i\int_0^t (\omega_k(t') - \Gamma_k(t'))dt'} |\psi_k(t)\rangle \tag{25.1}$$

where $|\psi_k(t)\rangle$ were normalized energy eigenkets for the (slowly) evolving Hamiltonian

$$H(t)|\psi_k(t)\rangle = E_k(t)|\psi_k(t)\rangle \tag{25.2}$$

In the problem sets we were shown a different adiabatic approximation, where are starting point is

$$|\psi(t)\rangle = \sum_k c_k(t)|\psi_k(t)\rangle\,. \tag{25.3}$$

For completeness, here is a walk through of the general amplitude derivation that is been used.

Guts We operate with our energy identity once again

$$\begin{aligned} 0 &= \left(H - i\hbar\frac{d}{dt}\right)\sum_k c_k|k\rangle \\ &= \sum_k c_k E_k|k\rangle - i\hbar c_k'|k\rangle - i\hbar c_k\left|k'\right\rangle, \end{aligned} \tag{25.4}$$

where

$$\left|k'\right\rangle = \frac{d}{dt}|k\rangle\,. \tag{25.5}$$

Bra'ing with $\langle m|$, and split the sum into $k = m$ and $k \neq m$ parts

$$0 = c_m E_m - i\hbar c_m' - i\hbar c_m\langle m|m'\rangle - i\hbar\sum_{k\neq m} c_k\langle m|k'\rangle \tag{25.6}$$

Again writing

$$\Gamma_m = i \langle m | m' \rangle \tag{25.7}$$

We have

$$c'_m = \frac{1}{i\hbar} c_m (E_m - \hbar\Gamma_m) - \sum_{k \neq m} c_k \langle m | k' \rangle , \tag{25.8}$$

In this form we can make an "Adiabatic" approximation, dropping the $k \neq m$ terms, and integrate

$$\int \frac{dc'_m}{c_m} = \frac{1}{i\hbar} \int_0^t (E_m(t') - \hbar\Gamma_m(t'))dt' \tag{25.9}$$

or

$$c_m(t) = A \exp\left(\frac{1}{i\hbar} \int_0^t (E_m(t') - \hbar\Gamma_m(t'))dt' \right). \tag{25.10}$$

Evaluating at $t = 0$, fixes the integration constant for

$$c_m(t) = c_m(0) \exp\left(\frac{1}{i\hbar} \int_0^t (E_m(t') - \hbar\Gamma_m(t'))dt' \right). \tag{25.11}$$

Observe that this is very close to the starting point of the adiabatic approximation we performed in class since we end up with

$$|\psi\rangle = \sum_k c_k(0) e^{-i \int_0^t (\omega_k(t') - \Gamma_k(t'))dt'} |k(t)\rangle , \tag{25.12}$$

So, to perform the more detailed approximation, that started with eq. (25.1), where we ended up with all the cross terms that had both ω_k and Berry phase Γ_k dependence, we have only to generalize by replacing $c_k(0)$ with $c_k(t)$.

Part V

APPENDICES

A

HARMONIC OSCILLATOR REVIEW

Consider

$$H_0 = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2 \tag{A.1}$$

Since it has been a while let us compute the raising and lowering factorization that was used so extensively for this problem.

It was of the form

$$H_0 = (aX - ibP)(aX + ibP) + \cdots \tag{A.2}$$

Why this factorization has an imaginary in it is a good question. It is not one that is given any sort of rationale in the text [4].

It is clear that we want $a = \sqrt{m/2}\omega$ and $b = 1/\sqrt{2m}$. The difference is then

$$H_0 - (aX - ibP)(aX + ibP) = -iab\,[X, P] = -i\frac{\omega}{2}\,[X, P] \tag{A.3}$$

That commutator is an $i\hbar$ value, but what was the sign? Let us compute so we do not get it wrong

$$\begin{aligned}
[x, p]\,\psi &= -i\hbar\,[x, \partial_x]\,\psi \\
&= -i\hbar(x\partial_x\psi - \partial_x(x\psi)) \\
&= -i\hbar(-\psi) \\
&= i\hbar\psi
\end{aligned} \tag{A.4}$$

So we have

$$H_0 = \left(\omega\sqrt{\frac{m}{2}}X - i\sqrt{\frac{1}{2m}}P\right)\left(\omega\sqrt{\frac{m}{2}}X + i\sqrt{\frac{1}{2m}}P\right) + \frac{\hbar\omega}{2} \tag{A.5}$$

Factoring out an $\hbar\omega$ produces the form of the Hamiltonian that we used before

$$H_0 = \hbar\omega\left(\left(\sqrt{\frac{m\omega}{2\hbar}}X - i\sqrt{\frac{1}{2m\hbar\omega}}P\right)\left(\sqrt{\frac{m\omega}{2\hbar}}X + i\sqrt{\frac{1}{2m\hbar\omega}}P\right) + \frac{1}{2}\right). \tag{A.6}$$

The factors were labeled the uppering ($a^\dagger$) and lowering (a) operators respectively, and written

$$\begin{aligned} H_0 &= \hbar\omega\left(a^\dagger a + \frac{1}{2}\right) \\ a &= \sqrt{\frac{m\omega}{2\hbar}}X + i\sqrt{\frac{1}{2m\hbar\omega}}P \\ a^\dagger &= \sqrt{\frac{m\omega}{2\hbar}}X - i\sqrt{\frac{1}{2m\hbar\omega}}P. \end{aligned} \tag{A.7}$$

Observe that we can find the inverse relations

$$\begin{aligned} X &= \sqrt{\frac{\hbar}{2m\omega}}\left(a + a^\dagger\right) \\ P &= i\sqrt{\frac{m\hbar\omega}{2}}\left(a^\dagger - a\right) \end{aligned} \tag{A.8}$$

Question What is a good reason that we chose this particular factorization? For example, a quick computation shows that we could have also picked

$$H_0 = \hbar\omega\left(aa^\dagger - \frac{1}{2}\right). \tag{A.9}$$

I do not know that answer. That said, this second factorization is useful in that it provides the commutator relation between the raising and lowering operators, since subtracting eq. (A.9) and eq. (A.7) yields

$$\left[a, a^\dagger\right] = 1. \tag{A.10}$$

If we suppose that we have eigenstates for the operator $a^\dagger a$ of the form

$$a^\dagger a\,|n\rangle = \lambda_n\,|n\rangle\,, \tag{A.11}$$

then the problem of finding the eigensolution of H_0 reduces to solving this problem. Because $a^\dagger a$ commutes with $1/2$, an eigenstate of $a^\dagger a$ is also an eigenstate of H_0. Utilizing eq. (A.10) we then have

$$\begin{aligned} a^\dagger a(a\,|n\rangle) &= (aa^\dagger - 1)a\,|n\rangle \\ &= a(a^\dagger a - 1)\,|n\rangle \\ &= a(\lambda_n - 1)\,|n\rangle \\ &= (\lambda_n - 1)a\,|n\rangle\,, \end{aligned} \tag{A.12}$$

so we see that $a\,|n\rangle$ is an eigenstate of $a^\dagger a$ with eigenvalue $\lambda_n - 1$.

Similarly for the raising operator

$$\begin{aligned} a^\dagger a(a^\dagger\,|n\rangle) &= a^\dagger(aa^\dagger)\,|n\rangle) \\ &= a^\dagger(a^\dagger a + 1)\,|n\rangle) \\ &= a^\dagger(\lambda_n + 1)\,|n\rangle), \end{aligned} \tag{A.13}$$

and find that $a^\dagger\,|n\rangle$ is also an eigenstate of $a^\dagger a$ with eigenvalue $\lambda_n + 1$.

Supposing that there is a lowest energy level (because the potential $V(x) = m\omega x^2/2$ has a lower bound of zero) then the state $|0\rangle$ for which the energy is the lowest when operated on by a we have

$$a\,|0\rangle = 0 \tag{A.14}$$

Thus

$$a^\dagger a\,|0\rangle = 0, \tag{A.15}$$

and

$$\lambda_0 = 0. \tag{A.16}$$

This seems like a small bit of slight of hand, since it sneakily supplies an integer value to λ_0 where up to this point 0 was just a label.

If the eigenvalue equation we are trying to solve for the Hamiltonian is

$$H_0\,|n\rangle = E_n\,|n\rangle\,. \tag{A.17}$$

Then we must then have

$$E_n = \hbar\omega\left(\lambda_n + \frac{1}{2}\right) = \hbar\omega\left(n + \frac{1}{2}\right) \tag{A.18}$$

B

VERIFYING THE HELMHOLTZ GREEN'S FUNCTION

Motivation In class this week, looking at an instance of the Helmholtz equation

$$\left(\boldsymbol{\nabla}^2 + \mathbf{k}^2\right)\psi_{\mathbf{k}}(\mathbf{r}) = s(\mathbf{r}). \tag{B.1}$$

We were told that the Green's function

$$\left(\boldsymbol{\nabla}^2 + \mathbf{k}^2\right)G^0(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \tag{B.2}$$

that can be used to solve for a particular solution this differential equation via convolution

$$\psi_{\mathbf{k}}(\mathbf{r}) = \int G^0(\mathbf{r}, \mathbf{r}')s(\mathbf{r}')d^3\mathbf{r}', \tag{B.3}$$

had the value

$$G^0(\mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi}\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}. \tag{B.4}$$

Let us try to verify this.
Application of the Helmholtz differential operator $\boldsymbol{\nabla}^2 + \mathbf{k}^2$ on the presumed solution gives

$$\left(\boldsymbol{\nabla}^2 + \mathbf{k}^2\right)\psi_{\mathbf{k}}(\mathbf{r}) = -\frac{1}{4\pi}\int\left(\boldsymbol{\nabla}^2 + \mathbf{k}^2\right)\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}s(\mathbf{r}')d^3\mathbf{r}'. \tag{B.5}$$

When $\mathbf{r} \neq \mathbf{r}'$ To proceed we will need to evaluate

$$\boldsymbol{\nabla}^2\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}. \tag{B.6}$$

Writing $\mu = |\mathbf{r} - \mathbf{r}'|$ we start with the computation of

$$\begin{aligned}\frac{\partial}{\partial x}\frac{e^{ik\mu}}{\mu} &= \frac{\partial\mu}{\partial x}\left(\frac{ik}{\mu} - \frac{1}{\mu^2}\right)e^{ik\mu} \\ &= \frac{\partial\mu}{\partial x}\left(ik - \frac{1}{\mu}\right)\frac{e^{ik\mu}}{\mu}\end{aligned} \tag{B.7}$$

We see that we will have

$$\boldsymbol{\nabla}\frac{e^{ik\mu}}{\mu} = \left(ik - \frac{1}{\mu}\right)\frac{e^{ik\mu}}{\mu}\boldsymbol{\nabla}\mu. \tag{B.8}$$

Taking second derivatives with respect to x we find

$$\begin{aligned}\frac{\partial^2}{\partial x^2}\frac{e^{ik\mu}}{\mu} &= \frac{\partial^2\mu}{\partial x^2}\left(ik - \frac{1}{\mu}\right)\frac{e^{ik\mu}}{\mu} + \frac{\partial\mu}{\partial x}\frac{\partial\mu}{\partial x}\frac{1}{\mu^2}\frac{e^{ik\mu}}{\mu} + \left(\frac{\partial\mu}{\partial x}\right)^2\left(ik - \frac{1}{\mu}\right)^2\frac{e^{ik\mu}}{\mu} \\ &= \frac{\partial^2\mu}{\partial x^2}\left(ik - \frac{1}{\mu}\right)\frac{e^{ik\mu}}{\mu} + \left(\frac{\partial\mu}{\partial x}\right)^2\left(-k^2 - \frac{2ik}{\mu} + \frac{2}{\mu^2}\right)\frac{e^{ik\mu}}{\mu}.\end{aligned} \tag{B.9}$$

Our Laplacian is then

$$\boldsymbol{\nabla}^2\frac{e^{ik\mu}}{\mu} = \left(ik - \frac{1}{\mu}\right)\frac{e^{ik\mu}}{\mu}\boldsymbol{\nabla}^2\mu + \left(-k^2 - \frac{2ik}{\mu} + \frac{2}{\mu^2}\right)\frac{e^{ik\mu}}{\mu}(\boldsymbol{\nabla}\mu)^2. \tag{B.10}$$

Now lets calculate the derivatives of μ. Working on x again, we have

$$\begin{aligned}\frac{\partial}{\partial x}\mu &= \frac{\partial}{\partial x}\sqrt{(x-x')^2 + (y-y')^2 + (z-z')^2} \\ &= \frac{1}{2}2(x-x')\frac{1}{\sqrt{(x-x')^2 + (y-y')^2 + (z-z')^2}} \\ &= \frac{x-x'}{\mu}.\end{aligned} \tag{B.11}$$

So we have

$$\begin{aligned}\boldsymbol{\nabla}\mu &= \frac{\mathbf{r}-\mathbf{r}'}{\mu} \\ (\boldsymbol{\nabla}\mu)^2 &= 1\end{aligned} \tag{B.12}$$

Taking second derivatives with respect to x we find

$$\begin{aligned}\frac{\partial^2}{\partial x^2}\mu &= \frac{\partial}{\partial x}\frac{x-x'}{\mu} \\ &= \frac{1}{\mu} - (x-x')\frac{\partial\mu}{\partial x}\frac{1}{\mu^2} \\ &= \frac{1}{\mu} - (x-x')\frac{x-x'}{\mu}\frac{1}{\mu^2} \\ &= \frac{1}{\mu} - (x-x')^2\frac{1}{\mu^3}.\end{aligned} \tag{B.13}$$

So we find

$$\boldsymbol{\nabla}^2\mu = \frac{3}{\mu} - \frac{1}{\mu}, \tag{B.14}$$

or

$$\boldsymbol{\nabla}^2\mu = \frac{2}{\mu}. \tag{B.15}$$

Inserting this and $(\boldsymbol{\nabla}\mu)^2$ into eq. (B.10) we find

$$\boldsymbol{\nabla}^2\frac{e^{ik\mu}}{\mu} = \left(ik - \frac{1}{\mu}\right)\frac{e^{ik\mu}}{\mu}\frac{2}{\mu} + \left(-k^2 - \frac{2ik}{\mu} + \frac{2}{\mu^2}\right)\frac{e^{ik\mu}}{\mu} \quad = -k^2\frac{e^{ik\mu}}{\mu} \tag{B.16}$$

This shows us that provided $\mathbf{r} \neq \mathbf{r}'$ we have

$$\left(\boldsymbol{\nabla}^2 + \mathbf{k}^2\right)G^0(\mathbf{r}, \mathbf{r}') = 0. \tag{B.17}$$

In the neighborhood of $|\mathbf{r} - \mathbf{r}'| < \epsilon$ Having shown that we end up with zero everywhere that $\mathbf{r} \neq \mathbf{r}'$ we are left to consider a neighborhood of the volume surrounding the point $\mathbf{r}$ in our integral. Following the Coulomb treatment in §2.2 of [11] we use a spherical volume element centered around $\mathbf{r}$ of radius ϵ, and then convert a divergence to a surface area to evaluate the integral away from the problematic point

$$-\frac{1}{4\pi}\int_{\text{all space}}\left(\boldsymbol{\nabla}^2 + \mathbf{k}^2\right)\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}s(\mathbf{r}')d^3\mathbf{r}' = -\frac{1}{4\pi}\int_{|\mathbf{r}-\mathbf{r}'|<\epsilon}\left(\boldsymbol{\nabla}^2 + \mathbf{k}^2\right)\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}s(\mathbf{r}')d^3\mathbf{r}' \tag{B.18}$$

We make the change of variables $\mathbf{r}' = \mathbf{r} + \mathbf{a}$. We add an explicit $\mathbf{r}$ suffix to our Laplacian at the same time to remind us that it is taking derivatives with respect to the coordinates of $\mathbf{r} = (x, y, z)$, and not the coordinates of our integration variable $\mathbf{a} = (a_x, a_y, a_z)$. Assuming sufficient continuity and "well behavedness" of $s(\mathbf{r}')$ we will be able to pull it out of the integral, giving

$$\begin{aligned}-\frac{1}{4\pi}\int_{|\mathbf{r}-\mathbf{r}'|<\epsilon}\left(\boldsymbol{\nabla}_\mathbf{r}^2 + \mathbf{k}^2\right)\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}s(\mathbf{r}')d^3\mathbf{r}' &= -\frac{1}{4\pi}\int_{|\mathbf{a}|<\epsilon}\left(\boldsymbol{\nabla}_\mathbf{r}^2 + \mathbf{k}^2\right)\frac{e^{ik|\mathbf{a}|}}{|\mathbf{a}|}s(\mathbf{r}+\mathbf{a})d^3\mathbf{a} \\ &= -\frac{s(\mathbf{r})}{4\pi}\int_{|\mathbf{a}|<\epsilon}\left(\boldsymbol{\nabla}_\mathbf{r}^2 + \mathbf{k}^2\right)\frac{e^{ik|\mathbf{a}|}}{|\mathbf{a}|}d^3\mathbf{a}\end{aligned} \tag{B.19}$$

Recalling the dependencies on the derivatives of $|\mathbf{r}-\mathbf{r}'|$ in our previous gradient evaluations, we note that we have

$$\begin{aligned}\boldsymbol{\nabla}_{\mathbf{r}}\left|\mathbf{r}-\mathbf{r}'\right| &= -\boldsymbol{\nabla}_{\mathbf{a}}|\mathbf{a}| \\ \left(\boldsymbol{\nabla}_{\mathbf{r}}\left|\mathbf{r}-\mathbf{r}'\right|\right)^2 &= \left(\boldsymbol{\nabla}_{\mathbf{a}}|\mathbf{a}|\right)^2 \\ \boldsymbol{\nabla}^2_{\mathbf{r}}\left|\mathbf{r}-\mathbf{r}'\right| &= \boldsymbol{\nabla}^2_{\mathbf{a}}|\mathbf{a}|,\end{aligned} \tag{B.20}$$

so with $\mathbf{a} = \mathbf{r}-\mathbf{r}'$, we can rewrite our Laplacian as

$$\boldsymbol{\nabla}^2_{\mathbf{r}}\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} = \boldsymbol{\nabla}^2_{\mathbf{a}}\frac{e^{ik|\mathbf{a}|}}{|\mathbf{a}|} = \boldsymbol{\nabla}_{\mathbf{a}}\cdot\left(\boldsymbol{\nabla}_{\mathbf{a}}\frac{e^{ik|\mathbf{a}|}}{|\mathbf{a}|}\right) \tag{B.21}$$

This gives us

$$\begin{aligned}-\frac{s(\mathbf{r})}{4\pi}\int_{|\mathbf{a}|<\epsilon}(\boldsymbol{\nabla}^2_{\mathbf{a}}+\mathbf{k}^2)\frac{e^{ik|\mathbf{a}|}}{|\mathbf{a}|}d^3\mathbf{a} &= -\frac{s(\mathbf{r})}{4\pi}\int_{dV}\boldsymbol{\nabla}_{\mathbf{a}}\cdot\left(\boldsymbol{\nabla}_{\mathbf{a}}\frac{e^{ik|\mathbf{a}|}}{|\mathbf{a}|}\right)d^3\mathbf{a} - \frac{s(\mathbf{r})}{4\pi}\int_{dV}\mathbf{k}^2\frac{e^{ik|\mathbf{a}|}}{|\mathbf{a}|}d^3\mathbf{a} \\ &= -\frac{s(\mathbf{r})}{4\pi}\int_{dA}\left(\boldsymbol{\nabla}_{\mathbf{a}}\frac{e^{ik|\mathbf{a}|}}{|\mathbf{a}|}\right)\cdot\hat{\mathbf{a}}d^2\mathbf{a} - \frac{s(\mathbf{r})}{4\pi}\int_{dV}\mathbf{k}^2\frac{e^{ik|\mathbf{a}|}}{|\mathbf{a}|}d^3\mathbf{a}\end{aligned} \tag{B.22}$$

To complete these evaluations, we can now employ a spherical coordinate change of variables. Let us do the $\mathbf{k}^2$ volume integral first. We have

$$\begin{aligned}\int_{dV}\mathbf{k}^2\frac{e^{ik|\mathbf{a}|}}{|\mathbf{a}|}d^3\mathbf{a} &= \int_{a=0}^{\epsilon}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\mathbf{k}^2\frac{e^{ika}}{a}a^2 da\sin\theta d\theta d\phi \\ &= 4\pi k^2\int_{a=0}^{\epsilon}ae^{ika}da \\ &= 4\pi\int_{u=0}^{k\epsilon}ue^{iu}du \\ &= 4\pi(-iu+1)e^{iu}\Big|_0^{k\epsilon} \\ &= 4\pi\left((-ik\epsilon+1)e^{ik\epsilon}-1\right)\end{aligned} \tag{B.23}$$

To evaluate the surface integral we note that we will require only the radial portion of the gradient, so have

$$\begin{aligned}\left(\boldsymbol{\nabla}_{\mathbf{a}}\frac{e^{ik|\mathbf{a}|}}{|\mathbf{a}|}\right)\cdot\hat{\mathbf{a}} &= \left(\hat{\mathbf{a}}\frac{\partial}{\partial a}\frac{e^{ika}}{a}\right)\cdot\hat{\mathbf{a}} \\ &= \frac{\partial}{\partial a}\frac{e^{ika}}{a} \\ &= \left(ik\frac{1}{a}-\frac{1}{a^2}\right)e^{ika} \\ &= (ika-1)\,\frac{e^{ika}}{a^2}\end{aligned} \tag{B.24}$$

Our area element is $a^2\sin\theta d\theta d\phi$, so we are left with

$$\begin{aligned}\int_{dA}\left(\boldsymbol{\nabla}_{\mathbf{a}}\frac{e^{ik|\mathbf{a}|}}{|\mathbf{a}|}\right)\cdot\hat{\mathbf{a}}d^2\mathbf{a} &= \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}(ika-1)\,\frac{e^{ika}}{a^2}a^2\sin\theta d\theta d\phi\Big|_{a=\epsilon} \\ &= 4\pi\,(ik\epsilon-1)\,e^{ik\epsilon}\end{aligned} \tag{B.25}$$

Putting everything back together we have

$$\begin{aligned}-\frac{1}{4\pi}\int_{\text{all space}}\left(\boldsymbol{\nabla}^2+\mathbf{k}^2\right)\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}s(\mathbf{r}')d^3\mathbf{r}' &= -s(\mathbf{r})\left((-ik\epsilon+1)e^{ik\epsilon}-1+(ik\epsilon-1)\,e^{ik\epsilon}\right) \\ &= -s(\mathbf{r})\left((-ik\epsilon+1+ik\epsilon-1)e^{ik\epsilon}-1\right)\end{aligned} \tag{B.26}$$

But this is just

$$\boxed{-\frac{1}{4\pi}\int_{\text{all space}}\left(\boldsymbol{\nabla}^2+\mathbf{k}^2\right)\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}s(\mathbf{r}')d^3\mathbf{r}' = s(\mathbf{r}).} \tag{B.27}$$

This completes the desired verification of the Green's function for the Helmholtz operator. Observe the perfect cancellation here, so the limit of $\epsilon\to 0$ can be independent of how large k is made. You have to complete the integrals for both the Laplacian and the $\mathbf{k}^2$ portions of the integrals and add them, before taking any limits, or else you will get into trouble (as I did in my first attempt).

C

EVALUATING THE SQUARED SINC INTEGRAL

In the Fermi's golden rule lecture we used the result for the integral of the squared sinc function. Here is a reminder of the contours required to perform this integral.

We want to evaluate

$$\int_{-\infty}^{\infty} \frac{\sin^2(x|\mu|)}{x^2} dx \tag{C.1}$$

We make a few change of variables

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{\sin^2(x|\mu|)}{x^2} dx &= |\mu| \int_{-\infty}^{\infty} \frac{\sin^2(y)}{y^2} dy \\ &= -i|\mu| \int_{-\infty}^{\infty} \frac{(e^{iy} - e^{-iy})^2}{(2iy)^2} i dy \\ &= -\frac{i|\mu|}{4} \int_{-i\infty}^{i\infty} \frac{e^{2z} + e^{-2z} - 2}{z^2} dz \end{aligned} \tag{C.2}$$

Now we pick a contour that is distorted to one side of the origin as in fig. C.1

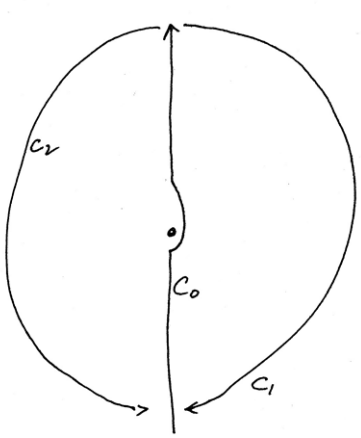

Figure C.1: Contour distorted to one side of the double pole at the origin

We employ Jordan's theorem (§8.12 [9]) now to pick the contours for each of the integrals since we need to ensure the $e^{\pm z}$ terms converges as $R \to \infty$ for the $z = Re^{i\theta}$ part of the contour. We can write

$$\int_{-\infty}^{\infty} \frac{\sin^2(x|\mu|)}{x^2} dx = -\frac{i|\mu|}{4} \left(\int_{C_0+C_2} \frac{e^{2z}}{z^2} dz + \int_{C_0+C_1} \frac{e^{-2z}}{z^2} dz - \int_{C_0+C_1} \frac{2}{z^2} dz \right) \tag{C.3}$$

The second two integrals both surround no poles, so we have only the first to deal with

$$\begin{aligned} \int_{C_0+C_2} \frac{e^{2z}}{z^2} dz &= 2\pi i \frac{1}{1!} \frac{d}{dz} e^{2z} \Big|_{z=0} \\ &= 4\pi i \end{aligned} \tag{C.4}$$

Putting everything back together we have

$$\int_{-\infty}^{\infty} \frac{\sin^2(x|\mu|)}{x^2} dx = -\frac{i|\mu|}{4} 4\pi i = \pi|\mu| \tag{C.5}$$

On the cavalier choice of contours The choice of which contours to pick above may seem pretty arbitrary, but they are for good reason. Suppose you picked $C_0 + C_1$ for the first integral. On the big C_1 arc, then with a $z = Re^{i\theta}$ substitution we have

$$\begin{aligned} \left| \int_{C_1} \frac{e^{2z}}{z^2} dz \right| &= \left| \int_{\theta=\pi/2}^{-\pi/2} \frac{e^{2R(\cos\theta + i\sin\theta)}}{R^2 e^{2i\theta}} Rie^{i\theta} d\theta \right| \\ &= \frac{1}{R} \left| \int_{\theta=\pi/2}^{-\pi/2} e^{2R(\cos\theta + i\sin\theta)} e^{-i\theta} d\theta \right| \\ &\leq \frac{1}{R} \int_{\theta=-\pi/2}^{\pi/2} \left| e^{2R\cos\theta} \right| d\theta \\ &\leq \frac{\pi e^{2R}}{R} \end{aligned} \tag{C.6}$$

This clearly doesn't have the zero convergence property that we desire. We need to pick the C_2 contour for the first (positive exponent) integral since in that $[\pi/2, 3\pi/2]$ range, $\cos\theta$ is always negative. We can however, use the C_1 contour for the second (negative exponent) integral. Explicitly, again by example, using C_2 contour for the first integral, over that portion of the arc we have

$$
\begin{aligned}
\left|\int_{C_2} \frac{e^{2z}}{z^2} dz\right| &= \left|\int_{\theta=\pi/2}^{3\pi/2} \frac{e^{2R(\cos\theta + i\sin\theta)}}{R^2 e^{2i\theta}} Rie^{i\theta} d\theta\right| \\
&= \frac{1}{R}\left|\int_{\theta=\pi/2}^{3\pi/2} e^{2R(\cos\theta + i\sin\theta)} e^{-i\theta} d\theta\right| \\
&\leq \frac{1}{R}\int_{\theta=\pi/2}^{3\pi/2} \left|e^{2R\cos\theta} d\theta\right| \\
&\approx \frac{1}{R}\int_{\theta=\pi/2}^{3\pi/2} \left|e^{-2R} d\theta\right| \\
&= \frac{\pi e^{-2R}}{R}
\end{aligned}
\tag{C.7}
$$

D

DERIVATIVE RECURRENCE RELATION FOR HERMITE POLYNOMIALS

For a QM problem I had need of a recurrence relation for Hermite polynomials. I found it in [1], but thought I had try to derive the relation myself.

The starting point I will use is the Rodgigues' formula definition of the Hermite polynomials

$$H_n = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2} \tag{D.1}$$

Let us write $D = d/dx$, and take the derivative of H_n

$$\begin{aligned}
(-1)^n DH_n &= D\left(e^{x^2} D^n e^{-x^2}\right) \\
&= 2xe^{x^2} D^n e^{-x^2} + e^{x^2} D^n \left(-2xe^{-x^2}\right) \\
&= 2xe^{x^2} D^n e^{-x^2} + e^{x^2} \sum_{k=0}^{n} \binom{n}{k} D^k(-2x) D^{n-k} e^{-x^2} \\
&= 2xe^{x^2} D^n e^{-x^2} + e^{x^2} \sum_{k=0}^{1} \binom{n}{k} D^k(-2x) D^{n-k} e^{-x^2} \\
&= \cancel{2xe^{x^2} D^n e^{-x^2}} + e^{x^2} \left(\cancel{-2xD^n e^{-x^2}} - 2nD^{n-1} e^{-x^2}\right) \\
&= -2nD^{n-1} e^{-x^2}
\end{aligned} \tag{D.2}$$

So we have the rather simple end result

$$\frac{d}{dx} H_n(x) = 2nH_{n-1}(x). \tag{D.3}$$

E

MATHEMATICA NOTEBOOKS

These Mathematica notebooks, some just trivial ones used to generate figures, others more elaborate, and perhaps some even polished, can be found in
https://raw.github.com/peeterjoot/mathematica/master/.

The free Wolfram CDF player, is capable of read-only viewing these notebooks to some extent.

Files saved explicitly as CDF have interactive content that can be explored with the CDF player.

- Sep 15, 2011 phy456/desai_S_24_2_1_verify.nb

  Some integrals related to QM hydrogen atom energy expectation values.

- Sep 24, 2011 phy456/problem_set_2,_problem_2,_verify_wavefunction_normalization.nb

  Some trig integrals that I didn't feel like doing manually.

- Sep 24, 2011 phy456/exponential_integrals.nb

  More gaussian integrals and some that Mathematica didn't know how to do.

- Sep 28, 2011 phy456/problem_set_3_integrals.nb

  Some Gaussian integrals.

- Oct 2, 2011 phy456/24.4.3_attempt_with_mathematica.nb

  Some variational method calculations for QM energy estimation.

- Oct 5, 2011 phy456/gaussian_fitting_for_abs_function.nb

  Hankle function fitting for e^-b|x| and related plots.

- Oct 6, 2011 phy456/stack_overflow_question_mathematica_exponential_Nth_derivative_treated_as_an_unknown_

  Stripped down example notebook for stackoverflow question about Derivative[2] not behaving well.

- Oct 6, 2011 phy456/stackoverflow_question_about_listable.nb

  Stripped down example notebook for stackoverflow question about Listable attribute defaults.

- Oct 8, 2011 phy456/qmTwoL8figures.nb

  Plot of gaussian weighted cosine, its Fourier transform, and figure for perturbation of Harmonic oscillator system.

- Oct 9, 2011 phy456/qmTwoL9figures.nb

  Sinusoid plot turned on at t_0 and ongoing from there.

- Oct 10, 2011 phy456/problem_set_4,_problem_2.nb

  Some trig integrals that Mathematica didn't evaluate correctly. Don't trust a tool without thinking whether the results are good!

- Oct 15, 2011 phy456/desai_24_4_4.nb

  Another worked variational method problem.

- Oct 15, 2011 phy456/desai_24_4_5.nb

  Another worked variational method problem.

- Oct 15, 2011 phy456/desai_24_4_6.nb

  Another worked variational method problem. Looks like I've learned about the /. operator for evaluating variables with values.

- Oct 15, 2011 phy456/qmTwoL10figures.nb

  Some sinc function plots. Learned how to use Manipulate to make sliders.

- Oct 16, 2011 phy456/desai_attempt_to_verify_section_16.3.nb

  Some energy expectation value calculations.

- Oct 17, 2011 phy456/qmTwoL11figures.nb

  Some vector addition and function translation figures.

- Oct 18, 2011 phy456/problem_set_5_integrals.nb

  Some integrals of first order linear polynomials.

- Oct 19, 2011 phy456/qmTwoL12_figures.nb

  Some step and rect function plots.

- Oct 31, 2011 phy456/plot_question.nb

  Another stackoverflow mathematica question. Why no output in my plot. Learned about Mathematica local and global variables as a result.

- Oct 31, 2011 phy456/problem_set_7_verify_rotation_matrix_orthonormal.nb

  A sanity check on a rotation matrix calculated as part of a problem set.

- Dec 17, 2011 phy456/qmTwoExamReflection.cdf

  Exam problem 2a. Calculate the matrix of a Perturbation Hamiltonian $-\boldsymbol{\mu}_d \cdot \mathbf{E}$ with respect to the $n = 2$ hydrogen atom wave functions.

- March 28, 2013 phy456/24.4.3.newAttempt.nb

  A new attempt at Desai 24.4.3 from scratch. This one has an error, as did the original. The original is now fixed.

Part VI

BIBLIOGRAPHY

BIBLIOGRAPHY

[1] M. Abramowitz and I.A. Stegun. *Handbook of mathematical functions with formulas, graphs, and mathematical tables*, volume 55. Dover publications, 1964. (Cited on page 287.)

[2] D. Bohm. *Quantum Theory*. Courier Dover Publications, 1989. (Cited on pages 92 and 241.)

[3] F.W. Byron and R.W. Fuller. *Mathematics of Classical and Quantum Physics*. Dover Publications, 1992. (Cited on page 220.)

[4] BR Desai. *Quantum mechanics with basic field theory*. Cambridge University Press, 2009. (Cited on pages xi, 5, 23, 24, 26, 37, 40, 47, 54, 57, 59, 70, 84, 87, 95, 99, 107, 119, 125, 133, 137, 139, 147, 150, 153, 157, 161, 171, 173, 178, 185, 193, 199, 213, 219, 233, 243, 257, 259, and 273.)

[5] C. Doran and A.N. Lasenby. *Geometric algebra for physicists*. Cambridge University Press New York, Cambridge, UK, 1st edition, 2003. (Cited on pages 69 and 149.)

[6] D.J. Griffiths. *Introduction to quantum mechanics*, volume 1. Pearson Prentice Hall, 2005. (Cited on page 107.)

[7] D. Hestenes. *New Foundations for Classical Mechanics*. Kluwer Academic Publishers, 1999. (Cited on pages 66 and 149.)

[8] JD Jackson. *Classical Electrodynamics*. John Wiley and Sons, 2nd edition, 1975. (Cited on page 208.)

[9] W.R. Le Page and W.R. LePage. *Complex Variables and the Laplace Transform for Engineers*. Courier Dover Publications, 1980. (Cited on page 284.)

[10] A. Messiah, G.M. Temmer, and J. Potter. *Quantum mechanics: two volumes bound as one*. Dover Publications New York, 1999. (Cited on pages 45 and 217.)

[11] M. Schwartz. *Principles of Electrodynamics*. Dover Publications, 1987. (Cited on page 279.)

[12] JR Taylor. *Scattering Theory: the Quantum Theory of Nonrelativistic Scattering*, volume 1. 1972. (Cited on page 217.)

[13] F.G. Tricomi. *Integral equations*. Dover Pubns, 1985. (Cited on page 70.)

[14] Wikipedia. *Adiabatic theorem — Wikipedia, The Free Encyclopedia*, 2011. URL //en.wikipedia.org/w/index.php?title=Adiabatic_theorem&oldid=447547448. [Online; accessed 9-October-2011]. (Cited on page 84.)

[15] Wikipedia. *Geometric phase — Wikipedia, The Free Encyclopedia*, 2011. URL //en.wikipedia.org/w/index.php?title=Geometric_phase&oldid=430834614. [Online; accessed 9-October-2011]. (Cited on page 90.)

[16] Wikipedia. *Bessel function — Wikipedia, The Free Encyclopedia*, 2011. URL http://en.wikipedia.org/w/index.php?title=Bessel_function&oldid=461096228. [Online; accessed 4-December-2011]. (Cited on page 207.)

[17] Wikipedia. *Spin.orbit interaction — Wikipedia, The Free Encyclopedia*, 2011. URL http://en.wikipedia.org/w/index.php?title=Spin%E2%80%93orbit_interaction&oldid=451606718. [Online; accessed 2-November-2011]. (Cited on page 155.)

[18] Wikipedia. *Steradian — Wikipedia, The Free Encyclopedia*, 2011. URL http://en.wikipedia.org/w/index.php?title=Steradian&oldid=462086182. [Online; accessed 4-December-2011]. (Cited on page 207.)

[19] Wikipedia. *WKB approximation — Wikipedia, The Free Encyclopedia*, 2011. URL http://en.wikipedia.org/w/index.php?title=WKB_approximation&oldid=453833635. [Online; accessed 19-October-2011]. (Cited on page 112.)

[20] Wikipedia. *Zeeman effect — Wikipedia, The Free Encyclopedia*, 2011. URL http://en.wikipedia.org/w/index.php?title=Zeeman_effect&oldid=450367887. [Online; accessed 15-September-2011]. (Cited on page 123.)