A Condensation of my notes for the sections the test will cover

5.   Identical Particles

5.1   Two-Particle Systems

Classically   *Quantum Mechanically*

$$E_{1,2} = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V_{1,2}$$ $$\frac{\hbar}{i}\frac{\partial}{\partial t} = \frac{-\hbar^2}{2m_1}\nabla_1^2 + \frac{-\hbar^2}{2m_2}\nabla_2^2 + V_{1,2}$$

$$\Psi_{1,2} = \Psi(\vec{r}_1, \vec{r}_2, t) \text{ where}$$

$$1 = \int\int|\Psi(\vec{r}_1, \vec{r}_2, t)|^2 dVol_1 dVol_2, \quad \langle p_1 \rangle = \int\int\Psi^*(\vec{r}_1, \vec{r}_2, t)\hat{p}_1\Psi(\vec{r}_1, \vec{r}_2, t)dVol_1 dVol_2, \text{ ectc.}$$

Correct Hydrogen

$$\hat{H}_H = \frac{\hat{p}_e^2}{2m_e} + \frac{\hat{p}_p^2}{2m_p} - \frac{e^2}{4\pi\varepsilon_o r} \quad \text{where } \vec{r} = \vec{r}_e - \vec{r}_p$$

or (the center of mass), the Hamiltonian can be rephrased as

$$\hat{H}_H = \frac{\hat{p}_R^2}{2(m_e + m_p)} + \frac{\hat{p}_r^2}{2\frac{m_p m_e}{m_p + m_e}} - \frac{e^2}{4\pi\varepsilon_o r} \quad \text{where } \vec{R} = \frac{m_e\vec{r}_e + m_p\vec{r}_p}{m_e + m_p}$$

Separable solution of form $\Psi_H = \Psi(\vec{R}, t)\Psi(\vec{r}, t)$.

5.1.1   Bosons and Fermions

Distinguishable

$$\psi_{1,2 \atop D} = \psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \quad \text{particles 1 \& 2 in states } a \text{ and } b, \text{ respectively}$$

Indistinguishable / Identical

$$\boxed{\psi_{1,2} = A(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_a(\vec{r}_2)\psi_b(\vec{r}_1))}$$

Observe that swapping particles

if we choose the + sign, $\psi_{2,1 \atop +} = \psi_{1,2 \atop +}$

if we choose the − sign, $\psi_{2,1 \atop -} = -\psi_{1,2 \atop -}$

Fermions, half-integer spin. Spin ½ (and 3/2, 5/2,…) particles (electrons, protons,…) must be combined in anti-symmetric states; if we include the freedom of spin, that may mean either plus sign combining spin options and negative sign in the spatial wavefunction or negative sign combining spin options and positive sign in the wave function.

Bosons, full-integer spin. Spin 0, and 1 (and 2, 3,…) particles must be combined in symmetric states; if we include the freedom of spin, that may mean either plus sign in combining spin options and plus sign in the spatial wavefunction or negative sign in combining spin options and negative sign in the spatial wave function.

Particles in the same state
Bosons and Bose-Einstein Condensate
For *Bosons* (with same spin orientation), there's no problem,
$$\psi_{1,2_B} = A\big(\psi_a(\vec{r}_1)\psi_a(\vec{r}_2) + \psi_a(\vec{r}_2)\psi_a(\vec{r}_1)\big) = 2A\,\psi_a(\vec{r}_2)\psi_a(\vec{r}_1)$$

Fermions and Pauli Exclusion Principle
However, for *Fermions,* things don't look so good,
$$\psi_{1,2_F} = A\big(\psi_a(\vec{r}_1)\psi_a(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_a(\vec{r}_1)\big) = 0$$

Considering Spin
spelling out the options:

Fermion:

$$\Psi_{1,2F} = \psi_{1,2_-}\chi_{triplet} = A\big(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_b(\vec{r}_2)\psi_a(\vec{r}_1)\big)\begin{cases}\uparrow_1\uparrow_2 \\ \frac{1}{\sqrt{2}}\big(\uparrow_1\downarrow_2 + \downarrow_1\uparrow_2\big) \\ \downarrow_1\downarrow_2\end{cases}$$

Or

$$\Psi_{1,2F} = \psi_{1,2_+}\chi_{singlet} = A\big(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_b(\vec{r}_2)\psi_a(\vec{r}_1)\big)\frac{1}{\sqrt{2}}\big(\downarrow_1\uparrow_2 - \uparrow_1\downarrow_2\big)$$

Boson:

$$\Psi_{1,2B} = \psi_{1,2_+}\chi_{triplet} = A\big(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_b(\vec{r}_2)\psi_a(\vec{r}_1)\big)\begin{cases}\uparrow_1\uparrow_2 \\ \frac{1}{\sqrt{2}}\big(\uparrow_1\downarrow_2 + \downarrow_1\uparrow_2\big) \\ \downarrow_1\downarrow_2\end{cases}$$

Or

$$\Psi_{1,2B} = \psi_{1,2_-}\chi_{singlet} = A\big(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_b(\vec{r}_2)\psi_a(\vec{r}_1)\big)\frac{1}{\sqrt{2}}\big(\downarrow_1\uparrow_2 - \uparrow_1\downarrow_2\big)$$

5.1.2 Exchange Forces

For two interacting particles, the strength of their interaction depends upon their separation; the average separation of the two particles, in turn, depends on whether they're in a symmetric or anti-symmetric combination (or are distinguishable). Thus the type of combination impacts their interaction.

Case 1: Distinguishable Particles

$$\psi_{1,2} = \psi_a(\vec{r}_1)\psi_b(\vec{r}_2)$$
$$_D$$

$$\left\langle \left\langle (x_1 - x_2)^2 \right\rangle_a \right\rangle_b = \left\langle \left\langle x_1^2 \right\rangle_a \right\rangle_b + \left\langle \left\langle x_2^2 \right\rangle_a \right\rangle_b - 2\left\langle \left\langle x_1 x_2 \right\rangle_a \right\rangle_b$$

Where, what I mean by this double-bracket notation is we've got both wavefunctions a and b in there.

$$\left\langle \left\langle x_1^2 \right\rangle_a \right\rangle_b = \int \psi_{1,2}{}^* x_1^2 \psi_{1,2} dVol_1 dVol_2 = \int \psi_a(\vec{r}_1)^* \psi_b(\vec{r}_2)^* x_1^2 \psi_a(\vec{r}_1)\psi_b(\vec{r}_2) dVol_1 dVol_2$$

$$= \int \psi_a(\vec{r}_1)^* x_1^2 \psi_a(\vec{r}_1) dVol_1 \int \psi_b(\vec{r}_2)^* \psi_b(\vec{r}_2) dVol_2 = \left\langle x^2 \right\rangle_a \left\langle \psi_b | \psi_b \right\rangle = \left\langle x^2 \right\rangle_a$$

Working it out,

$$\left\langle (x_1 - x_2)^2 \right\rangle_{a,b} = \left\langle x^2 \right\rangle_a + \left\langle x^2 \right\rangle_b - 2\left\langle x \right\rangle_a \left\langle x \right\rangle_b$$
$$_D$$

Case 2: Identical Particles

$$\psi_{1,2} = \tfrac{1}{\sqrt{2}}\left(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)\right)$$
$$_{\pm}$$

Working this out, you get something very similar to the distinguishable case, but with an extra term,

$$\boxed{\left\langle (x_1 - x_2)^2 \right\rangle_{a,b \atop \pm} = \left\langle (x_1 - x_2)^2 \right\rangle_{a,b \atop D} \mp 2\left| \left\langle x \right\rangle_{ba} \right|^2}$$

The moral is that if the two indistinguishable particles are in anti-symmetric spatial state, they are *further* apart than if they were distinguishable, but if they are in the symmetric spatial state, then they are *closer* than if they were distinguishable.

Covalent bonds.

Recall that spin-1/2 particles can be in the symmetric spatial state if they are in the anti-symmetric, i.e., singlet, anti-aligned, spin state. So, in that case, two electrons shared by two atoms would tend *toward* each other, bridging the gap between the two atoms.

You may recall that Moore argued this would be the lower-energy configuration since being symmetric means that the shared wavefunction *doesn't* have to go to 0 in the middle, so the wavelength can by broader / the concavity can be less / the kinetic energy can be less.

5.2   Atoms

Qualitatively use the following knowledge to understand atoms
    a. Electronic wavefunctions for Hydrogen

b. How angular momentum freedoms mix (be they the l and s of an individual electron or the l's and s's of a pair of electrons)
c. The need for over-all anti-symmetric (upon exchange) multi-electron states
d. That anti-symmetric / symmetric *spatial* states on average have the electrons closer to / further from each other.

Approximating that the nucleus is stationary and nothing's changing inside of it, the interesting terms in the energy expression are for the electrons' kinetic and potential energies:

Classically   *Quantum Mechanically*

$$E_{atomic-electrons} \approx \sum_{j}^{Z}\left\{T_{e.j} - \frac{1}{4\pi\varepsilon_o}\frac{Ze^2}{r_j} + \sum_{k>j}^{Z}\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r_{j,k}}\right\} \qquad \frac{\hbar}{i}\frac{\partial}{\partial t} \approx \sum_{j}^{Z}\left\{\frac{-\hbar^2}{2m_e}\nabla_j^2 - \frac{1}{4\pi\varepsilon_o}\frac{Ze^2}{r_j} + \sum_{k>j}^{Z}\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r_{j,k}}\right\}$$

The solutions will depend upon the positions of all the electrons as well as their spins,

$$\Psi(\vec{r}_1,\vec{r}_2,...\vec{r}_Z,t)\chi(\vec{s}_1,\vec{s}_2,...\vec{s}_Z)$$

Combined Electron Wavefunction Symmetry
While two electrons *can* be in the same spatial state (characterized by quantum numbers n, l, m_l) if their spins combine in the singlet state (net spin = 0), as long as the spatial states don't have different energies, it's energetically favorable to be in *different* spatial states with an *anti-symmetric* combination because then the spins must be in a *symmetric* (triplet) state which, by the exchange-force argument, means they average a bit further apart and thus their mutual repulsion is weaker. So, the order in which (energy) degenerate states get filled is first all spins aligned, then start putting occupying the anti-aligned states – one of Hund's rules.

Electron-Electron Potential Effect
Aside from determining the order in which energy-degenerate states are occupied, what's the more obvious / classical effect of the electron-electron interaction?
From the perspective of a given electron, to the extent that other electrons are outside its orbit and have a spherically symmetric distribution, they have no effect on it; and to the extent that others are spherically-symmetrically distributed *inside* its orbit, the shield the equivalent number of protons. So an approximation for the Hamiltonian of the jth electron is

$$\hat{H}_j \approx \frac{-\hbar^2}{2m_e}\nabla_j^2 - \frac{1}{4\pi\varepsilon_o}\frac{Z_{eff.j}e^2}{r_j}$$

Where $Z_{eff.j}$ accounts for the shielding due to the other electrons inside its orbit. Of course, this has the form of the Hydrogen atom's Hamiltonian (with a factor of Z_{eff} on the e^2), so a reasonable 1st-order approximation for the energies and 1st-order approximation for the wavefunctions is simply the energies and wavefunctions for hydrogen, but with $Z_{eff}e^2$ everywhere there used to just be an e^2 in the equations.

5.2.1 Helium

In the case of Helium, there are two distinct electronic states with the same spatial wavefunctions (differing only by having opposite spin). By the above argument, the 0th-order approximate Hamiltonian for one of the electrons is simply

$$\frac{\hbar}{i}\frac{\partial}{\partial t} \approx \left(\frac{-\hbar^2}{2m_e}\nabla_1^2 - \frac{1}{4\pi\varepsilon_o}\frac{2e^2}{r_1}\right)$$

(the 1st-order correction replaces 2 with Z_{eff} which differs by about a fifth).

0th-Order Approximate Helium Ground State

For example, putting both electrons at the lowest energy state possible, $n = 1$ (which dictates $l = m = 0$ since $|m| \leq l < n$),

$$\psi_o(\vec{r}_1,\vec{r}_2)\chi(\vec{s}_1,\vec{s}_2) = \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)|1,0\rangle \text{ where } |1,0\rangle = \frac{1}{\sqrt{2}}\left(\uparrow\downarrow - \downarrow\uparrow\right)$$

Where $\boxed{\psi_{100}(\vec{r}_1) = \frac{1}{\sqrt{\pi a_{He}^3}}e^{-r/a_{He}} = \frac{2}{\sqrt{\pi a^3/2}}e^{-2r/a}}$ since $\boxed{a_{He} = \frac{4\pi\varepsilon_o\hbar^2}{m_e 2e^2} = \frac{1}{2}a}$

So $\psi_o(\vec{r}_1,\vec{r}_2)\chi(\vec{s}_1,\vec{s}_2) = \frac{8}{\pi a^3}e^{-2(r_1+r_2)/a}|1,0\rangle$

Similarly, $E_{He} \approx -\frac{2e^2}{8\pi\varepsilon_o a_{He}} - \frac{2e^2}{8\pi\varepsilon_o a_{He}} = -\frac{2e^2}{4\pi\varepsilon_o a_{He}} = -\frac{4e^2}{4\pi\varepsilon_o a} = -8\cdot 13.6eV = -109eV$

0th-order Approximate Helium Excited State

$$\psi(\vec{r}_1,\vec{r}_2)\chi(\vec{s}_1,\vec{s}_2) = A\left(\psi_{100}(\vec{r}_1)\psi_{n_b l_b m_b}(\vec{r}_2) \pm \psi_{n_b l_b m_b}(\vec{r}_1)\psi_{100}(\vec{r}_2)\right)\chi_{\mp}(\vec{s}_1,\vec{s}_2)$$

And $E_{He} \approx 4\left(\frac{-13.6eV}{n_1^2} + \frac{-13.6eV}{n_2^2}\right)$

Generally, greater separation / lower total energy if symmetric spin combination, spin triplet state (para-helim) than anti-symmetric spin combination, spin singlet state (ortho-helium)

5.2.2 The Periodic Table

We extend this kind of reasoning to consider multi-electron atoms. Now, the first-order picture is to imagine building atoms of Hydrogen-like orbitals, each of which must respect

$|m| \leq l < n$ which adds up to there being $2n^2$ 'slots' for electrons with a given n. Where the energy of an electron in a given level is approximately

$$E_{e_j} \approx -\frac{m}{2\hbar^2}\left(\frac{Z_{eff.j}e^2}{4\pi\varepsilon_o}\right)$$

where $Z_{eff.j}$ is roughly the number of electron states of higher n that are occupied (since that's the number of unshielded protons)

Filling Orbitals

There are some rules of thumb for the order in which hydrogen-like states get occupied in atoms. **Hund's first rule:** because of the "exchange force", energy-degenerate states get occupied with spins aligned first (and thus anti-symmetric spatially, and furthest apart.)

Hund's second rule: each orbiting electron constitutes a current loop, and as you should know from Phys 232, the lowest-energy configuration for current loops is being aligned, so states with orbital angular momentum aligned are filled first (and, as you should also know from Phys 232, magnetic interactions are weaker than electric ones, so Hund's first rule, which follows from electron-electron electric interaction, takes precedence over Hund's second.)

Hund's third rule: As we'll see in section 6.3, it's lowest energy to have spin and orbit anti-aligned (from the electron's perspective, the proton orbits it, so that constitutes another current loop to align with; however, since the spinning electron and orbiting proton have opposite signs, aligning the current loops means anti-aligning the angular momenta.)

As protons and electrons are added to build heavier atoms, keep in mind that two things dictate how atoms interact with each other: the number of energy-degenerate states that are unoccupied and the shape of the orbitals that reach out the furthest (generally determined by the Y_l^m of the largest n occupied states) so different elements that are similar in these two ways will interact similarly.

5.3   Solids

5.3.1 The Free Electron Gas

To 0th order, from the perspective of one electron in this solid, all the other electrons and all the protons in the nucleus all but cancel each other out; the electron's trapped in the solid, but other than that, it's free to zip around however it wants within the solid – like a gas particle in a box.

$$\psi(x,y,z) = \left(\sqrt{\tfrac{8}{V}}\,\sin(k_{n_x}x)\sin(k_{n_y}y)\sin(k_{n_z}z)\right) \text{ and } E = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) \text{ where } k_{n_j} \equiv \tfrac{n_j\pi}{l_j}$$

Where each n can be 1,2,3,4,… and for each of these spatial states there are two spin states.

Fermi Energy

You won't be asked anything from this section since it's dealt with more in Phys 344, and I'll leave it to that class.

The argument goes like this:
If you map out the possible states according to possible k combinations,

$$\frac{2\,states}{\Delta V_k} \qquad \text{where} \qquad \Delta V_k = \Delta k_x \Delta k_y \Delta k_z = \frac{\pi^3}{V}$$

The density of states in "k-space" is then
$$\frac{2\,states}{\Delta V_k} = \frac{N_e}{V_k}$$

$$E_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right), \text{ or } \sqrt{2mE_F}\,/\hbar = k_F = \sqrt{k_x^2 + k_y^2 + k_z^2} \,,$$

Is the radius of a sphere in k-space; all states with k combinations that lie within that sphere are occupied; all outside that sphere are empty.

Of course, the volume of a sphere of radius k_F is $V_{k.sphere} = \frac{4}{3}\pi k_F^3$, but looking at our grid of allowed states, we only have positive k components, so only the positive octant of the sphere encloses states.

$$V_k = \frac{1}{8}\left(\frac{4}{3}\pi k_F^3\right) = \frac{1}{6}\pi\left(\sqrt{2mE_F}\,/\hbar^2\right)^3 = \frac{1}{6}\pi\frac{\left(2mE_F\right)^{3/2}}{\hbar^3}$$

so

$$\frac{2\,states}{\Delta V_k} = \frac{N_e}{V_k} \text{ becomes } \frac{2}{\dfrac{\pi^3}{V}} = \frac{N_e}{\dfrac{1}{6}\pi\dfrac{\left(2mE_F\right)^{3/2}}{\hbar^3}} \text{ so } E_F = \frac{\hbar^2}{2m}\left(3\pi^2\frac{N_e}{V}\right)^{2/3} \text{ or if } q \text{ electrons per}$$

each of N atoms, $E_F = \dfrac{\hbar^2}{2m}\left(3\pi^2 q\dfrac{N}{V}\right)^{2/3}$

Ground State Energy

$$E_{total} = \sum_k E(k)\frac{states}{\Delta V_k}\Delta V_k \Rightarrow \int_0^{k_F} E(k)\left(\frac{states}{\Delta V_k}\right)dV_k$$

$$E_{total} = \int_0^{k_F}\frac{\hbar^2}{2m}k^2\left(\frac{2}{\frac{\pi^3}{V}}\right)\frac{1}{8}\left(4\pi k^2\right)dk = \left(\frac{V\hbar^2}{2m\pi^2}\right)\int_0^{k_F}k^4 dk = \frac{1}{5}\left(\frac{V\hbar^2}{2m\pi^2}\right)k_F^5 = \frac{3qN}{5\pi^{5/3}}E_F$$

For Pressure,
$$\Delta E_{total} = W = -P\Delta V$$
So, in the differential limit,

$$P = -\frac{dE_{total}}{dV} = -\frac{d}{dV}\left(\frac{\hbar^2}{10m\pi^{1/3}}\right)\frac{(3qN)^{5/3}}{V^{2/3}} = \frac{2}{3}\left(\frac{\hbar^2}{10m\pi^{1/3}}\right)\left(\frac{3qN}{V}\right)^{5/3} = \frac{2}{15\pi}\left(\frac{\hbar^2}{2m\pi^{1/3}}\right)\left(\frac{3qN}{V}\right)^{5/3}$$

5.3.2 Band Structure

The next simplest model is to allow that these valance electrons probably *do* notice the periodic placement of the atoms, and so would experience a periodic potential. Just to show how periodicity leads to bands of allowed states, Griffiths looks at the simplest imaginable periodic potential – a 1-D line of delta-potentials that wraps around on itself.

$$V(x) = \sum_{j=0}^{N-1} \delta(x - ja)$$

That the Hamiltonian is periodic constrains that the probability density is periodic which in turn constrains that the wavefunction is periodic *to within a phase*.

$$\psi(x+a) = e^{i\gamma}\psi(x)$$

To make life really simple, we imagine that we have a ring of N steps of length a, then looping all the way around would bring you back to where you started and looking at the exact same wavefunction:

$$\psi(x+Na) = \left(e^{i\gamma}\right)^N\psi(x) = \psi(x)$$

So it must be that $e^{iN\gamma} = 1$ or $N\gamma = n2\pi \Rightarrow \gamma = \frac{n2\pi}{N}$ for $n = \pm 0,1,2,3,\ldots$

So,

$$\boxed{\psi(x+a) = e^{in\frac{2\pi}{N}}\psi(x)}$$ for $n = \pm 1,2,3,\ldots$

Focusing on two adjacent cells and doing the usual thing of imposing boundary conditions:
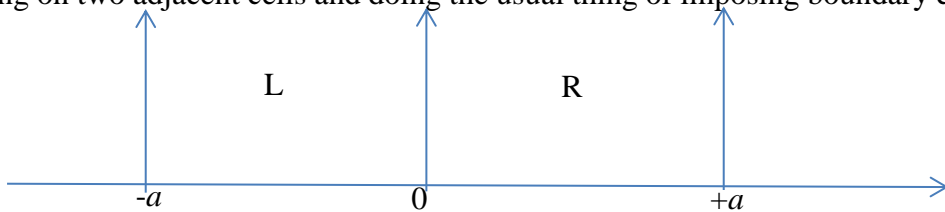
$$\psi_R(x) = Ae^{ikx} + Be^{-ikx} \text{ where } E = \frac{-\hbar^2 k^2}{2m}$$

The requirement $e^{in\frac{2\pi}{N}}\psi_L(x) = \psi_R(x+a)$ means $\psi_L(x) = e^{-in\frac{2\pi}{N}}\left(Ae^{ik(x+a)} + Be^{-ik(x+a)}\right)$

Boundary conditions

$$\psi_R(0) = \psi_L(0)$$

$$\left.\frac{d\psi_R}{dx}\right|_0 - \left.\frac{d\psi_L}{dx}\right|_0 = \frac{2m\alpha}{\hbar^2}\psi(0)$$

$$A + B = e^{-in\frac{2\pi}{N}}\left(Ae^{ik(a)} + Be^{-ik(a)}\right)$$

$$ik(A-B) - ike^{-in\frac{2\pi}{N}}\left(Ae^{ik(a)} - Be^{-ik(a)}\right) = \frac{2m\alpha}{\hbar^2}(A+B)$$

Phrase in terms of A/B, and combine to eliminate A/B:

$$\boxed{\cos(ka) + \frac{m\alpha}{k\hbar^2}\sin(ka) = \cos\left(n\frac{2\pi}{N}\right)}$$

Griffiths argues that, while the right hand side is inherently bound by +/- 1, the left hand side wouldn't be, thus this equation places constraints on the range of allowed k values. There are 'bands' of allowed k values and 'gaps' of un-allowed values. Looking at the threshold, where the equation = 1, you can guess a solution without too much trouble: if $k = n\,2\pi/a$. This corresponds with the wavefunction's simply being sinusoidal.

8. WKB Approximation

8.1 The "Classical" Region

Phrasing the wavefunction in the form $\psi(x) = A(x)e^{\pm ikx}$ for $E > V$, $k = \sqrt{2m(E-V)}/\hbar$

And writing the Schrodinger equation in the from $-\hbar^2 \dfrac{\partial^2 \psi}{\partial x^2} = 2m(E - V(x))\psi \equiv p^2(x)\psi$

We find
$$\left[i(\phi''A + 2\phi'A') + \left(A'' - (\phi')^2 A + \frac{p^2(x)}{\hbar^2} A \right) \right] e^{i\phi} = 0$$

Or
$$\phi''A + 2\phi'A' = 0 \quad \text{and} \quad A'' - (\phi')^2 A + \frac{p^2(x)}{\hbar^2} A = 0$$

Assume that A"/A << than the other terms, $\boxed{\psi(x) = A(x)e^{i\phi(x)} \approx \dfrac{C}{\sqrt{p(x)}} e^{\pm i \int_{x_o}^{x} p(x')dx'/\hbar}}$ where

$$\boxed{p(x) \equiv \sqrt{2m(E-V)}}$$

Example 8.1 Bumpy-bottomed infinite-square well

$$V(x) = \begin{cases} V_{in}(x) & \text{in box} \\ \infty & \text{out of box} \end{cases}$$

Guess $\psi(x) \approx \dfrac{1}{\sqrt{p(x)}} \left(C_+ e^{+i\phi(x)} + C_- e^{-i\phi(x)} \right) = \dfrac{1}{\sqrt{p(x)}} \left(C_s \sin(\phi(x)) + C_c \cos(\phi(x)) \right)$

$$\phi(x) \approx \int_0^x p(x')dx'/\hbar, \text{ which means } \phi(0) \approx \int_0^0 p(x')dx'/\hbar = 0$$

Boundary Conditions

$$\psi(0) \approx \frac{1}{\sqrt{p(0)}} (C_c) = 0 \text{ so } C_c = 0. \text{ Thus } \psi(x) \approx \frac{C_s \sin(\phi(x))}{\sqrt{p(x)}}$$

$$\psi(a) \approx \frac{C_s \sin(\phi(a))}{\sqrt{p(a)}} = 0 \text{ so } \phi(a) \approx \int_0^a p(x')dx'/\hbar = n\pi$$

Example 1.b

Say that $V(x) = \tfrac{1}{2}m\omega^2 x^2$, so $p(x) = \sqrt{2m\left(E - \tfrac{1}{2}m\omega^2 x^2\right)}$

And $\phi(x) \approx \int_0^x \sqrt{2m\left(E - \tfrac{1}{2}m\omega^2 x'^2\right)}dx'/\hbar = \sqrt{2mE}/\hbar \int_0^x \sqrt{\left(1 - \dfrac{m\omega^2 x'^2}{2E}\right)}dx'$

$$= \frac{2E}{\hbar\omega}\frac{1}{2}\left[\sqrt{1-\frac{m}{2E}\omega^2 x^2}\sqrt{\frac{m}{2E}}\omega x + \sin^{-1}\left(\sqrt{\frac{m}{2E}}\omega x\right)\right]$$

$$\phi(a) \approx \int_0^a p(x')dx'/\hbar = n\pi \quad \text{means} \quad \frac{1}{\hbar}\left[\sqrt{\frac{mE}{2}a^2 - \left(\frac{m}{2}\right)^2\omega^2 a^4} + \frac{E}{\hbar\omega}\sin^{-1}\left(\sqrt{\frac{m}{2E}}\omega a\right)\right] = n\pi$$

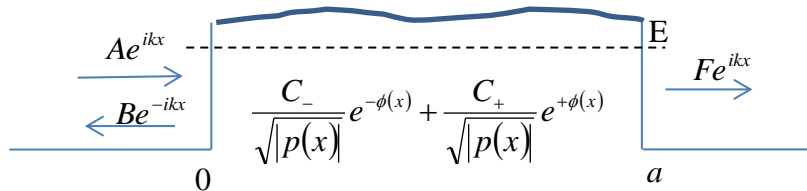Not pretty. Transendental relation that sets the allowed E values.

8.2   Tunneling

When V > E, we could run through the same argument, but then pop on the world at the end that, oops, V > E, so

$$p(x) = \sqrt{2m(E-V(x))} = i\sqrt{2m(V(x)-E)}$$

Which leads to

$$\boxed{\psi(x) \approx \frac{C}{\sqrt{|p(x)|}}e^{\pm\int_{x_o}^x |p(x')|dx'/\hbar}}$$

Usual wave-meets-barrier setup:

Now, we *can* use the WKB approach to find an expression for the wavefunction within the barrier. However, Griffiths uses it to give a ballpark approximation for the particular question of tunneling through a barrier. His argument is that, as we know, the transmission coefficient is

$$T = \left|\frac{F}{A}\right|^2 \approx \left|\frac{\dfrac{C_-}{\sqrt{|p(a)|}}e^{-\phi(a)}}{\dfrac{C_-}{\sqrt{|p(0)|}}e^{-\phi(0)}}\right|^2 = \left|\frac{\sqrt{|p(0)|}}{\sqrt{|p(a)|}}e^{-(\phi(a)-\phi(0))}\right|^2 = \frac{|p(0)|}{|p(a)|}e^{-2(\phi(0)-\phi(a))} = \sqrt{\frac{V(0)-E}{V(a)-E}}e^{-2\int_0^a |p(x')|dx'/\hbar}$$

Griffiths ignores the prefactor (indeed, it would cause real trouble), and focuses just on the exponential.

$$\boxed{T = \left|\frac{F}{A}\right|^2 \propto e^{-2\int_0^a |p(x')|dx'/\hbar}}$$

Example: STM, sloped barrier

In scanning tunneling microscopy, the electric field between tip and sample translates into a roughly linear voltage / potential. $V(x) = V(0) - bx$.

$$\int_0^a |p(x)| dx = \int_0^a \left| \sqrt{2m(V(x) - E)} \right| dx = \ldots = -\frac{2}{3} \sqrt{2mb} \left(\left(\frac{V(0) - E}{b} - a \right)^{3/2} - \left(\frac{V(0) - E}{b} \right)^{3/2} \right)$$

Since this appears in the exponent, this shows the exponential dependence on the separation of tip and sample, a.

Example 8.2 Gamow's theory of Alpha Decay

Applies the tunneling WKB approximation to find the exponential factor for tunneling through a repulsive Coulomb potential: $V(x) = \dfrac{Z}{4\pi\varepsilon_o} \dfrac{1}{x}$ and gets a functional dependence that agrees with experiment.

6. Time-Independent Perturbation Theory

6.1　Non-degenerate Perturbation Theory

6.1.1　General Formulation

If $\hat{H} = \hat{H}^o + \lambda(t)\hat{H}'$

Then $\psi_n = \psi_n^o + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \lambda^3\psi_n^{(3)} + ...$ and $E_n = E_n^o + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + ...$

and　　$\hat{H}\psi_n = E_n\psi_n$ becomes

$$\left(\hat{H}^o + \lambda\hat{H}'\right)\left(\psi_n^o + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \lambda^3\psi_n^{(3)} + ...\right) = \left(E_n^o + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + ..\right)\left(\psi_n^o + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \lambda^3\psi_n^{(3)} + ..\right)$$

Multiplying this out and expressing in terms of powers of λ,

$$0^{th}\ \text{order}:\ \hat{H}^o\psi_n^o = E_n^o\psi_n^o$$
$$1^{st}\ \text{order}:\ \hat{H}^o\psi_n^{(1)} + \hat{H}'\psi_n^o = E_n^o\psi_n^{(1)} + E_n^{(1)}\psi_n^o$$
$$2^{nd}\ \text{order}:\ \hat{H}^o\psi_n^{(2)} + \hat{H}'\psi_n^{(1)} = E_n^o\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^o$$

...

6.1.2　First-Order Theory

1st-order Energy $E_n^{(1)}$ Correction.
If we inner-product it with the known ψ_n^o, we have

$$\left\langle\psi_n^o\left|\hat{H}^o\psi_n^{(1)}\right\rangle + \left\langle\psi_n^o\left|\hat{H}'\psi_n^o\right\rangle = \left\langle\psi_n^o\left|E_n^o\psi_n^{(1)}\right\rangle + \left\langle\psi_n^o\left|E_n^{(1)}\psi_n^o\right\rangle\right.\right.\right.\right.$$

Or using that H is Hermitian on the left and pulling out constants on the right,

$$\left\langle\hat{H}^o\psi_n^o\left|\psi_n^{(1)}\right\rangle + \left\langle\psi_n^o\left|\hat{H}'\psi_n^o\right\rangle = E_n^o\left\langle\psi_n^o\left|\psi_n^{(1)}\right\rangle + E_n^{(1)}\right.\right.\right.$$

$$E_n^o\left\langle\psi_n^o\left|\psi_n^{(1)}\right\rangle + \left\langle\psi_n^o\left|\hat{H}'\psi_n^o\right\rangle = E_n^o\left\langle\psi_n^o\left|\psi_n^{(1)}\right\rangle + E_n^{(1)}\right.\right.\right.$$

Now we can cancel the first term from left and right to be left with

$$\boxed{\left\langle\psi_n^o\left|\hat{H}'\psi_n^o\right\rangle = E_n^{(1)}\right.}$$

Example:

$$\hat{H} = \hat{H}^o + \hat{H}' = \begin{pmatrix} V_o & 0 & 0 \\ 0 & -2V_o & 0 \\ 0 & 0 & 3V_o \end{pmatrix} + \begin{pmatrix} -\varepsilon & \varepsilon & 0 \\ \varepsilon & -\varepsilon & 0 \\ 0 & 0 & 0 \end{pmatrix}\ \text{For which}\ \left|\psi_1^o\right\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}\ \left|\psi_2^o\right\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}\ \left|\psi_3^o\right\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

$$E_1^{(1)} = \left\langle\psi_1^{(o)}\left|\hat{H}'\right|\psi_1^{(o)}\right\rangle = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix}\begin{pmatrix} -\varepsilon & \varepsilon & 0 \\ \varepsilon & -\varepsilon & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = -\varepsilon\ \text{so,}\ E_1 \approx E_1^{(o)} + E_1^{(1)} = V_o - \varepsilon\text{, etc.}$$

Example: An electron in a 1-D solid with a voltage applied, i.e., a sloped bottom.

$$\hat{H}'(x) = -e\Delta V \tfrac{x}{a}$$

$$E_n^{(1)} = \left\langle \psi_n^{(o)} \left| \hat{H}' \right| \psi_n^{(o)} \right\rangle = \int_0^a \left(\sqrt{\tfrac{2}{a}} \sin\left(\tfrac{n\pi}{a} x \right) \right)\left(-e\Delta V \tfrac{x}{a} \right)\left(\sqrt{\tfrac{2}{a}} \sin\left(\tfrac{n\pi}{a} x \right) \right) dx = \ldots = -\frac{e\Delta V}{2}\left(1 + \tfrac{1}{n\pi} \right)$$

So, the energy for each state, to first order correction, is

$$E_n \approx E_n^{(o)} + E_n^{(1)} = \frac{\hbar^2}{2m}\left(\frac{n\pi}{a} \right)^2 - \frac{e\Delta V}{2}\left(1 + \tfrac{1}{n\pi} \right)$$

1st-order Wavefunction $\psi_n^{(1)}$

The unperturbed wavefunctions are a complete basis set, so we should be able to express the 1st-order correction in terms of them,

$$\psi_n^{(1)} = \sum_{m \neq n} c_{n,m} \psi_m^{(o)} \quad \text{where} \quad \left\langle \psi_m^{(o)} \middle| \psi_n^{(1)} \right\rangle = c_{n,m}$$

Then rewriting the first-order expression as $\left(\hat{H}^o - E_n^o \right)\psi_n^{(1)} = \left(E_n^{(1)} - \hat{H}' \right)\psi_n^o$

And taking the inner product with $\psi_m^{(o)}$,

$$\left\langle \psi_m^o \middle| \left(\hat{H}^o - E_n^o \right)\psi_n^{(1)} \right\rangle = \left\langle \psi_m^o \middle| \left(E_n^{(1)} - \hat{H}' \right)\psi_n^o \right\rangle$$

$$\left\langle \hat{H}^o \psi_m^o \middle| \psi_n^{(1)} \right\rangle - E_n^o \left\langle \psi_m^o \middle| \psi_n^{(1)} \right\rangle = E_n^{(1)} \left\langle \psi_m^o \middle| \psi_n^o \right\rangle - \left\langle \psi_m^o \middle| \hat{H}' \psi_n^o \right\rangle$$

$$E_m^o \left\langle \psi_m^o \middle| \psi_n^{(1)} \right\rangle - E_n^o \left\langle \psi_m^o \middle| \psi_n^{(1)} \right\rangle = E_n^{(1)} 0 - \left\langle \psi_m^o \middle| \hat{H}' \psi_n^o \right\rangle$$

$$\left\langle \psi_m^o \middle| \psi_n^{(1)} \right\rangle = \frac{\left\langle \psi_m^o \middle| \hat{H}' \psi_n^o \right\rangle}{E_n^o - E_m^o}$$

And that is $\left\langle \psi_m^{(o)} \middle| \psi_n^{(1)} \right\rangle = c_{n,m}$

So

$$\boxed{\psi_n^{(1)} = \sum_{m \neq n} \frac{\left\langle \psi_m^o \middle| \hat{H}' \psi_n^o \right\rangle}{E_n^o - E_m^o} \psi_m^{(o)}}$$

Exercise: What's the first-order correction to the first eigenvector if ?

$$\hat{H} = \hat{H}^o + \hat{H}' = \begin{pmatrix} V_o & 0 & 0 \\ 0 & -2V_o & 0 \\ 0 & 0 & 3V_o \end{pmatrix} + \begin{pmatrix} -\varepsilon & \varepsilon & 0 \\ \varepsilon & -\varepsilon & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \left| \psi_1^o \right\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \ \left| \psi_2^o \right\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \ \left| \psi_3^o \right\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

So the two inner products are

$$\left\langle \psi_2^{(o)} \left| \hat{H}' \right| \psi_1^{(o)} \right\rangle = \begin{pmatrix} 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} -\varepsilon & \varepsilon & 0 \\ \varepsilon & -\varepsilon & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} -\varepsilon \\ \varepsilon \\ 0 \end{pmatrix} = \varepsilon$$

$$\left\langle \psi_3^{(o)} \left| \hat{H}' \right| \psi_1^{(o)} \right\rangle = ... = 0$$

So, the sum is

$$\psi_1^{(1)} = \sum_{m \neq 1} \frac{\left\langle \psi_m^o \left| \hat{H}' \psi_1^o \right\rangle\right.}{E_1^o - E_m^o} \psi_m^{(o)} = \frac{\left\langle \psi_2^o \left| \hat{H}' \psi_1^o \right\rangle\right.}{E_1^o - E_2^o} \psi_2^{(o)} + \frac{\left\langle \psi_3^o \left| \hat{H}' \psi_1^o \right\rangle\right.}{E_1^o - E_3^o} \psi_2^{(o)} = \frac{\varepsilon}{V_o - (-2V_o)} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} + \frac{0}{V_o - 3V_o} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{\varepsilon}{3V_o} \\ 0 \end{pmatrix}$$

Then, to first order,

$$\left| \psi_1 \right\rangle \approx \left| \psi_1^o \right\rangle + \left| \psi_1^{(1)} \right\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ \frac{\varepsilon}{3V_o} \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ \frac{\varepsilon}{3V_o} \\ 0 \end{pmatrix}$$

Exercise: Or, with the sloped bottom in a square well,

$$\hat{H}'(x) = -e\Delta V \frac{x}{a}, \qquad \left| \psi_n^o \right\rangle = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right), \text{ and } \qquad E_n^{(o)} = \frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2$$

So, $\left\langle \psi_m^{(o)} \left| \hat{H}' \right| \psi_n^{(o)} \right\rangle = \int_0^a \left(\sqrt{\frac{2}{a}} \sin\left(\frac{m\pi}{a} x\right)\right)\left(-e\Delta V \frac{x}{a}\right)\left(\sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right)\right)dx = ... = e\Delta V \frac{8}{\pi^2} \frac{mn}{(m^2 - n^2)}$ for m±n odd;

    0 for m±n even.

Then $\psi_n^{(1)} = \sum_{m \neq n} \frac{\left\langle \psi_m^o \left| \hat{H}' \psi_n^o \right\rangle\right.}{E_n^o - E_m^o} \psi_m^{(o)} = \sqrt{\frac{2}{a}} \frac{16ma^2}{\hbar^2 \pi^4} e\Delta V \sum_{\substack{m \neq n \\ odd\, m\pm n}} \frac{mn \sin\left(\frac{m\pi}{a} x\right)}{\left(m^2 - n^2\right)^2}$

6.1.3 Second-Order Theory

$$\hat{H}^o \psi_n^{(2)} + \hat{H}' \psi_n^{(1)} = E_n^o \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^o$$

2st-order Energy En(2) Correction.

$$\left\langle \psi_n^o \left| \hat{H}^o \psi_n^{(2)} \right\rangle + \left\langle \psi_n^o \left| \hat{H}' \psi_n^{(1)} \right\rangle = \left\langle \psi_n^o \left| E_n^o \psi_n^{(2)} \right\rangle + \left\langle \psi_n^o \left| E_n^{(1)} \psi_n^{(1)} \right\rangle + \left\langle \psi_n^o \left| E_n^{(2)} \psi_n^o \right\rangle\right.\right.\right.\right.\right.$$

$$E_n^o \left\langle \psi_n^o \left| \psi_n^{(2)} \right\rangle + \left\langle \psi_n^o \left| \hat{H}' \psi_n^{(1)} \right\rangle = E_n^o \left\langle \psi_n^o \left| \psi_n^{(2)} \right\rangle + E_n^{(1)} \left\langle \psi_n^o \left| \psi_n^{(1)} \right\rangle + E_n^{(2)}\right.\right.\right.\right.$$

The left most terms on both sides are equal and so cancel

$$\left\langle \psi_n^o \left| \hat{H}' \psi_n^{(1)} \right\rangle = E_n^{(1)} \left\langle \psi_n^o \left| \psi_n^{(1)} \right\rangle + E_n^{(2)}\right.\right.$$

But $\psi_n^{(1)} = \sum_{m \neq n} c_{n,m} \psi_m^{(o)}$. So $\left\langle \psi_n^o \left| \psi_n^{(1)} \right\rangle = 0\right.$.

Leaving $\left\langle \psi_n^o \left| \hat{H}' \psi_n^{(1)} \right\rangle = E_n^{(2)}\right.$

since $\psi_n^{(1)} = \sum_{m \neq n} \frac{\left\langle \psi_m^o \left| \hat{H}' \psi_n^o \right\rangle\right.}{E_n^o - E_m^o} \psi_m^{(o)}$, we can write this as

$$\left\langle \psi_n^o \left| \hat{H}' \sum_{m \neq n} \frac{\left\langle \psi_m^o \left| \hat{H}' \psi_n^o \right.\right\rangle}{E_n^o - E_m^o} \psi_m^{(o)} \right.\right\rangle = E_n^{(2)}$$

$$\sum_{m \neq n} \frac{\left\langle \psi_m^o \left| \hat{H}' \psi_n^o \right.\right\rangle}{E_n^o - E_m^o} \left\langle \psi_n^o \left| \hat{H}' \psi_m^{(o)} \right.\right\rangle = E_n^{(2)}$$

$$\boxed{\sum_{m \neq n} \frac{\left| \left\langle \psi_m^o \left| \hat{H}' \psi_n^o \right.\right\rangle \right|^2}{E_n^o - E_m^o} = E_n^{(2)}}$$

6.2   Degenerate Perturbation Theory

6.2.1 Two-Fold Degeneracy

Say both ψ_{na}^o and ψ_{nb}^o have energy E_n^o when subject to $\hat{H}^o$. Some linear combination of them (which also has this energy) will evolve smoothly to a maximal/minimal new energy when the perturbation is turned on,

$$\boxed{\psi_n^o = \alpha \psi_{na}^o + \beta \psi_{nb}^o}$$

1st-order energy correction

$$\left\langle \psi_{na}^o \left| \hat{H}^o \right| \psi_n^{(1)} \right\rangle + \left\langle \psi_{na}^o \left| \hat{H}' \right| \psi_n^o \right\rangle = E_n^o \left\langle \psi_{na}^o \left\| \psi_n^{(1)} \right.\right\rangle + E_n^{(1)} \left\langle \psi_{na}^o \left\| \psi_n^o \right.\right\rangle$$

Which reduces to $\left\langle \psi_{na}^o \left| \hat{H}' \right| \psi_n^o \right\rangle = E_n^{(1)} \left\langle \psi_{na}^o \left\| \psi_n^o \right.\right\rangle$

substituting in $\psi_n^o = \alpha \psi_{na}^o + \beta \psi_{nb}^o$, leads to $\alpha \left\langle \psi_{na}^o \left| \hat{H}' \right| \psi_{na}^o \right\rangle + \beta \left\langle \psi_{na}^o \left| \hat{H}' \right| \psi_{nb}^o \right\rangle = \alpha E_n^{(1)}$

Similarly, $\alpha \left\langle \psi_{nb}^o \left| \hat{H}' \right| \psi_{na}^o \right\rangle + \beta \left\langle \psi_{nb}^o \left| \hat{H}' \right| \psi_{nb}^o \right\rangle = \beta E_n^{(1)}$

Naming these inner products $W_{ba} \equiv \left\langle \psi_{nb}^o \left| \hat{H}' \right| \psi_{na}^o \right\rangle$, $W_{aa} \equiv \left\langle \psi_{na}^o \left| \hat{H}' \right| \psi_{na}^o \right\rangle$, $W_{bb} \equiv \left\langle \psi_{nb}^o \left| \hat{H}' \right| \psi_{nb}^o \right\rangle$

The two algebraic relations can be phrased efficiently as a single matrix relation,

$$\begin{array}{l} \alpha W_{aa} + \beta W_{ab} = \alpha E_n^{(1)} \\ \alpha W_{ba} + \beta W_{bb} = \beta E_n^{(1)} \end{array} \quad \text{or} \quad \begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E_n^{(1)} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

Solving the characteristic equation for this matrix gives
Which is solved by the quadratic equation

$$\boxed{E_{n\pm}^{(1)} = \frac{1}{2} \left[W_{bb} + W_{aa} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right]}$$

And then $\boxed{\beta_\pm = \alpha_\pm \dfrac{E_{n_\pm}^{(1)} - W_{aa}}{W_{ab}}}$ can be used to relate the coefficients

Exercise: returning to this, What are the energies of the 'good' eigenvectors for the two degenerate states?

$$\hat{H} = \hat{H}^o + \hat{H}' = \begin{pmatrix} V_o & 0 & 0 \\ 0 & -2V_o & 0 \\ 0 & 0 & V_o \end{pmatrix} + \begin{pmatrix} -\varepsilon & \varepsilon & 0 \\ \varepsilon & -\varepsilon & 0 \\ 0 & 0 & 0 \end{pmatrix}, \; \left| \psi_1^o \right\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \; \left| \psi_2^o \right\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \text{ and } \left| \psi_3^o \right\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

Find W_{11}, W_{33}, and W_{13}

$$W_{11} = \left\langle \psi_1^{(o)} \left| \hat{H}' \right| \psi_1^{(o)} \right\rangle = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} -\varepsilon & \varepsilon & 0 \\ \varepsilon & -\varepsilon & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = -\varepsilon$$

Etc.

Put together to get the two energies

$$E_{n\pm}^{(1)} = \frac{1}{2}\left[W_{bb} + W_{aa} \pm \sqrt{\left(W_{aa} - W_{bb}\right)^2 + 4\left|W_{ab}\right|^2} \right]$$

Griffith's Theorem

If you can find an operator that commutes with the perturbed H, and which has distinct eigenvalues, then its eigenfunctions are the "good" ones (recall, commuting with the Hamiltonian means that the operator's eigen values remain constant in time.)   This ends up being very handy when we're thinking about corrections for the Hydrogen atom.

6.2.2 Higher Order Degeneracy

So, the way we set up the problem for doubly-degenerate clearly generalizes; if we have more than two states with the same energies under the original Hamiltonian, we can solve for the multiple 'good' eigenvectors and their first-order energy corrections by solving the matrix problem

$$\begin{pmatrix} W_{aa} & W_{ab} & W_{ac} & \cdots \\ W_{ba} & W_{bb} & W_{bc} & \cdots \\ W_{ca} & W_{cb} & W_{cc} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \chi \\ \cdots \end{pmatrix} = E_n^{(1)} \begin{pmatrix} \alpha \\ \beta \\ \chi \\ \cdots \end{pmatrix} \quad \text{where this is a Hermitian matrix since } W_{ab} = W_{ba}^*$$

6.3   The Fine Structure of Hydrogen

6.3.1 The Relativistic Kinetic Correction

$$T = E - E_{rest} \text{ so } T = \sqrt{(pc)^2 + (mc^2)^2} - mc^2 = mc^2\left(\sqrt{\left(\frac{p}{mc}\right)^2 + 1} - 1 \right) = \frac{1}{2}\frac{p^2}{2m} - \frac{1}{8}\frac{p^4}{m^3c^2} + \dots$$

So, the perturbation would be $\boxed{\hat{H}'' = -\dfrac{\hat{p}^4}{8m^3c^2}}$

and non-degenerate 1st-order Perturbation Theory would give us

$$E_n^{(1)^r} = \left\langle \psi_n^o \left| \hat{H}' \right| \psi_n^o \right\rangle = \left\langle \psi_n^o \left| -\frac{p^4}{8m^3c^2} \right| \psi_n^o \right\rangle = -\frac{\left\langle \psi_n^o \left| p^4 \right| \psi_n^o \right\rangle}{8m^3c^2}$$

where $\hat{p}^2\psi_n^o = 2m\left(E_n^o - V(r)\right)\psi_n^o$ so

$$\hat{p}^4\psi_n^o = \hat{p}^2 2m\left(E_n^o - V(r)\right)\psi_n^o = \hbar\frac{2me^2}{\varepsilon_o}\delta^3(r)\psi_n^o + \left(2m\left(E_n^o - V(r)\right)\right)^2\psi_n^o$$

Thus

$$E_n^{(1)r} = -\frac{\hbar e^2\left\langle\psi_n^o\left|\delta^3(r)\right|\psi_n^o\right\rangle}{4m^2c^2\varepsilon_o} - \frac{\left\langle\psi_n^o\left|\left(E_n^o - V\right)^2\right|\psi_n^o\right\rangle}{2mc^2}$$

For all but $l = 0$ solutions, the wavefunction is 0 at r=0, so the first term vanishes, leaving

$$E_n^{(1)r} = -\frac{1}{2mc^2}\left\langle\psi_n^o\left|\left(E_n^o\right)^2 - 2E_n^oV + (V)^2\right|\psi_n^o\right\rangle$$

$$E_n^{(1)r} = -\frac{1}{2mc^2}\left(\left(E_n^o\right)^2 - 2E_n^o\left\langle\psi_n^o\left|V\right|\psi_n^o\right\rangle + \left\langle\psi_n^o\left|(V)^2\right|\psi_n^o\right\rangle\right)$$

Then being explicit about our potential,

$$E_n^{(1)r} = -\frac{1}{2mc^2}\left(\left(E_n^o\right)^2 - 2E_n^o\left\langle\psi_n^o\left|\frac{-e^2}{4\pi\varepsilon_o r}\right|\psi_n^o\right\rangle + \left\langle\psi_n^o\left|\left(\frac{-e^2}{4\pi\varepsilon_o r}\right)^2\right|\psi_n^o\right\rangle\right)$$

Which becomes

$$E_n^{(1)r} = -\frac{1}{2mc^2}\left(\left(E_n^o\right)^2 + \frac{e^2 E_n^o}{2\pi\varepsilon_o}\frac{1}{n^2 a} + \left(\frac{e^2}{4\pi\varepsilon_o}\right)^2\frac{1}{\left(l+\frac{1}{2}\right)n^3 a^2}\right)$$

And that can be re-expressed as

$$\boxed{E_n^{(1)r} = -\frac{\left(E_n^o\right)^2}{2mc^2}\left(\frac{4n}{\left(l+\frac{1}{2}\right)} - 3\right)}$$

6.3.2 The Relativistic Potential Correction: Spin-Orbit Coupling

Correcting the potential energy term too, to account for the electron's moving, gives. A quantitative/qualitative argument about looking at the situation from the perspective of a co-orbiting reference frame gets all the right physical parameters, but correcting a few factors of 2 is beyond the scope of this course.

$$\boxed{\hat{H}'^{so} \approx \frac{e^2}{8\pi\varepsilon_o}\frac{\hat{S}\cdot\hat{L}}{(mc)^2 r^3}}$$

$\hat{S}^2, \hat{L}^2, \hat{J} = \hat{L} + \hat{S}$ all commute with this new operator (while $\hat{S}_z, \hat{L}_z$ do *not*), their eigen vectors are 'good', with their eigen values, *l, s,* and *j.*

So, finding the expected correction for the 'good' eigenfunctions:

$$E^{(1)so} = \left\langle\psi_{jls}\left|\hat{H}'^{so}\right|\psi_{jls}\right\rangle = \left\langle\frac{e^2}{8\pi\varepsilon_o}\frac{\hat{S}\cdot\hat{L}}{(mc)^2 r^3}\right\rangle = \frac{e^2}{8\pi\varepsilon_o(mc)^2}\left\langle\hat{S}\cdot\hat{L}\right\rangle\left\langle\frac{1}{r^3}\right\rangle$$

$$E^{(1)so} == \frac{e^2}{8\pi\varepsilon_o (mc)^2} \frac{\langle \hat{S} \cdot \hat{L} \rangle}{l(l+\frac{1}{2})(l+1)n^3 a^3}$$

As for $\langle \hat{S} \cdot \hat{L} \rangle$,

Since $\hat{J} = \hat{L} + \hat{S}$, we can say that $\hat{J}^2 = (\hat{L} + \hat{S}) \cdot (\hat{L} + \hat{S}) = \hat{L}^2 + \hat{S}^2 + \hat{L} \cdot \hat{S} + \hat{S} \cdot \hat{L}$,

Then $\langle \hat{S} \cdot \hat{L} \rangle = \frac{1}{2} \left(\langle \hat{J}^2 \rangle - \langle \hat{L}^2 \rangle - \langle \hat{S}^2 \rangle \right) = \frac{1}{2} \left(j(j+1) - l(l+1) - s(s+1) \right) \hbar^2$

So, $E^{(1)so} = \frac{e^2}{8\pi\varepsilon_o (mc)^2} \frac{\frac{1}{2}\left(j(j+1) - l(l+1) - s(s+1) \right)\hbar^2}{l(l+\frac{1}{2})(l+1)n^3 a^3}$

using that s = ½ we get the surprisingly simple $\boxed{E^{(1)fs} = E^{(1)so} + E^{(1)r} = \frac{(E_n)^2}{2mc^2}\left(3 - \frac{4n}{j+\frac{1}{2}} \right)}$

6.4   The Zeeman Effect

A current loop constitutes a magnetic dipole, and the energy associated with a magnetic dipole's alignment with an external magnetic field is

$$\boxed{\hat{H}^Z = -\hat{\mu}_e \cdot \vec{B}_{ext} = -\left(\hat{\mu}_{orbit} + \hat{\mu}_{spin} \right) \cdot \vec{B}_{ext} = \frac{e}{2m}\left(\hat{L} + 2\hat{S} \right) \cdot \vec{B}_{ext}}$$

We now have two distinct perturbations on top of the simple hamiltonian which we've solved,

$$\hat{H} = \qquad \hat{H}^o \qquad + \qquad\qquad \hat{H}^{r.T\&V} \qquad\qquad + \qquad \hat{H}^Z$$
$$\hat{H} = \qquad \hat{H}^o \qquad + \quad \hat{H}^r \; + \qquad \hat{H}^{so} \qquad + \qquad \hat{H}^Z$$
$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_o r} - \frac{\hat{p}^4}{8m^3 c^2} + \frac{e^2}{8\pi\varepsilon_o}\frac{\hat{S}\cdot\hat{L}}{(mc)^2 r^3} + \frac{e}{2m}\left(\hat{L} + 2\hat{S} \right)\cdot \vec{B}_{ext}$$

So, we want an approximate expression for the energies that the Hydrogen atom can have.

The approach is,
$$\hat{H} = \hat{H}^o + \hat{H}'^{bigger} + \hat{H}'^{smaller}$$
$$E \approx E^o + \langle \psi_{good.for.big} | \hat{H}'^{bigger} + \hat{H}'^{smaller} | \psi_{good.for.big} \rangle$$

6.4.2   Strong-Field Zeeman Effect

Now, if the Zeeman Effect is the stronger of the two, then the system can't be approximated as being isolated and the total angular momentum can't be approximated as being conserved $-j$ isn't a good eigen value. However, the spin and orbital angular momentum *will* keep their alignment with the external magnetic field, so m_l and m_s are good eigen values which implies

that l and s must be too (can't very well have the magnitude of the angular momenta change but not the projection on the z-axis.) so the good states are $\left|n,l,m_l,s,m_s\right\rangle$.

So

$$E^Z \approx \left\langle n,l,m_l,s,m_s\left|\frac{e}{2m}\left(\hat{L}_z+2\hat{S}_z\right)B_{ext}\right|n,l,m_l,s,m_s\right\rangle = \frac{e}{2m}\left(m_l\hbar+2m_s\hbar\right)B_{ext}$$

$$\boxed{E^Z = \frac{e\hbar B_{ext}}{2m}\left(m_l+2m_s\right)}$$

That said, we should really go back and rethink the spin-orbit correction in terms of *this* basis set.

$$E^{(1)so} \approx \left\langle n,l,m_l,s,m_s\left|\hat{H}'^{so}\right|n,l,m_l,s,m_s\right\rangle = \left\langle n,l,m_l,s,m_s\left|\frac{e^2}{8\pi\varepsilon_o}\frac{\hat{S}\cdot\hat{L}}{\left(mc\right)^2 r^3}\right|n,l,m_l,s,m_s\right\rangle$$

$$= \frac{e^2}{8\pi\varepsilon_o\left(mc\right)^2}\left\langle n,l,m_l,s,m_s\left|\frac{\hat{S}_x\hat{L}_x+\hat{S}_y\hat{L}_y+\hat{S}_z\hat{L}_z}{r^3}\right|n,l,m_l,s,m_s\right\rangle$$

For the denominator, the same argument applies as did before,

$$\left\langle\frac{1}{r^3}\right\rangle = \frac{1}{l\left(l+\frac{1}{2}\right)\left(l+1\right)n^3 a^3}$$

But now, the x and y components of the spin and orbital angular momentum are not defined; indeed, there's no reason for the system to prefer one orientation or another, and we have two independent a cones of possible S and L values, visualized by
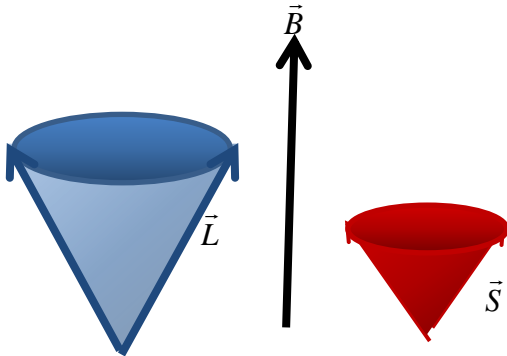
So we don't really have to do the integrals to find the expectation values for the x and y components of the angular momenta, they're going to average out to

$$\left\langle\hat{S}_x\right\rangle = \left\langle\hat{L}_x\right\rangle = \left\langle\hat{S}_y\right\rangle = \left\langle\hat{L}_y\right\rangle = 0$$

Which just leaves

$$\left\langle\hat{S}_z\hat{L}_z\right\rangle = m_s\hbar m_l\hbar$$

So, in the strong-field limit,

$$E^{(1)so} = \frac{e^2}{8\pi\varepsilon_o\left(mc\right)^2}\frac{m_s m_l\hbar^2}{l\left(l+\frac{1}{2}\right)\left(l+1\right)n^3 a^3}$$

Or using $E_o^o = -\frac{1}{2}\frac{e^2}{4\pi\varepsilon_o a}\frac{1}{n^2}$ to write this a little neater

$$E^{(1)so} = -E_n^0 \left(\frac{\hbar}{mca} \right)^2 \frac{m_s m_l}{l\left(l + \frac{1}{2}\right)(l+1)n}$$

Both relativistic corrections / fine-structure corrections together give

$$\boxed{E^{(1)fine} = \frac{|E_o^o|\alpha^2}{n^3} \left(\frac{3}{4n} - \frac{l(l+1) - m_s m_l}{l\left(l + \frac{1}{2}\right)(l+1)} \right)}$$

6.4.1   Weak-Field Zeeman Effect

Now, if the external magnetic field is quite weak, our system is *nearly* isolated, so the total angular momentum (both magnitude, quantized by j and direction, quantized by m_j) must remain *nearly* constant. Furthermore, we'd found that S and L commuted with the spin-orbit energy term, so s and l (though not m_s and m_l) remain constant too, so the "good" states are $\left| n, j, m_j, l, s \right\rangle$

$$E^Z \approx \left\langle n, j, m_j, l, s \left| \frac{e}{2m} \left(\hat{L}_z + 2\hat{S}_z \right) B_{ext} \right| n, j, m_j, l, s \right\rangle$$

Rewriting the operator in terms of operators for the good states, $\left(\hat{L}_z + 2\hat{S}_z \right) = \hat{J}_z + \hat{S}_z$
And we can reason out the expectation value for / average of Sz graphically,

If the *length and direction* of J are set, and the *lengths* of L and S are set, and $J = L + S$, then we have a cone of possible S and L values, visualized by
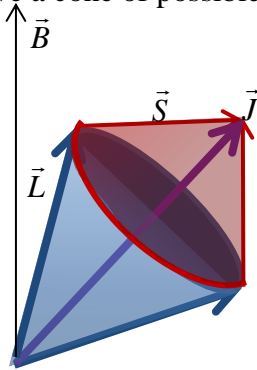
On average, whatever components S has that are perpendicular to J average out to 0, leaving only its projection in the J direction. That is to say $\vec{S}_{ave} = \left(\vec{S} \cdot \frac{\vec{J}}{|J|} \right) \frac{\vec{J}}{|J|}$

$$\left\langle \hat{S}_z \right\rangle = \left\langle \left(\frac{\hat{S} \cdot \hat{J}}{\hat{J}^2} \right) \hat{J}_z \right\rangle = \frac{\left\langle \hat{S} \cdot \hat{J} \right\rangle}{j(j+1)\hbar^2} m_j \hbar \quad \text{wher} \quad L^2 = \left(\vec{J} - \vec{S} \right)^2 = J^2 + S^2 - 2\vec{S} \cdot \vec{J} \Rightarrow \vec{S} \cdot \vec{J} = \frac{J^2 + S^2 - L^2}{2}$$

Of course, s isn't much of a variable, s = ½, so ½ (½ +1) = ¾

$$\left\langle \hat{S}_z \right\rangle = \frac{\left\langle J^2 + S^2 - L^2 \right\rangle}{2j(j+1)\hbar^2} m_j \hbar = \frac{j(j+1) - l(l+1) + \frac{3}{4}}{2j(j+1)} m_j \hbar$$

There we have it,

$$E^Z \approx \left\langle n, j, m_j, l, s \left| \frac{e}{2m} (J_z + S_z) B_{ext} \right| n, j, m_j, l, s \right\rangle$$

$$\boxed{E^Z \approx \frac{eB_{ext}}{2m} \left(1 + \frac{j(j+1) - l(l+1) + \frac{3}{4}}{2j(j+1)} \right) m_j \hbar}$$

6.4.3   Intermediate-Field Zeeman Effect

Time for Degenerate perturbation Theory and constructing the W matrix using $W_{ab} = \left\langle \psi_a \left| H' \right| \psi_b \right\rangle$. Thanks to the Clebsch-Gordan table, we can express the wavefunctions either in terms of j and m_j or in terms of l, m_l, s, m_s. So, we have

$$\left| \psi \right\rangle_a = \left| j, m_j \right\rangle_a = c_{1,a} \left| l, m_l \right\rangle_{1a} \left| s, m_s \right\rangle_{1a} + c_2 \left| l, m_l \right\rangle_{2a} \left| s, m_s \right\rangle_{2a} + \ldots$$

Then

$$W_{ab} = \left\langle \psi_a \left| H' \right| \psi_b \right\rangle = \left\langle \psi_a \left| H'^{fine} + H'^Z \right| \psi_b \right\rangle = \left\langle \psi_a \left| H'^{fine} \right| \psi_b \right\rangle + \left\langle \psi_a \left| H'^Z \right| \psi_b \right\rangle = W_{ab}^{fine} + W_{ab}^Z$$

Let's see how one would build the W matrix Griffiths gives.

Looking at just a couple of terms will give the idea of how it works.

$$W_{7,8}^Z = \left\langle \psi_7 \left| H'^Z \right| \psi_8 \right\rangle$$

Since

$$H'^Z = \frac{eB_{ext}}{2m} \hat{L}_z + 2\hat{S}_z$$

We'll want to express the two states in terms of L_z and S_z's (ortho-normal) eigen vectors.

$$W_{7,8}^Z = \left\langle \psi_7 \left| H'^Z \right| \psi_8 \right\rangle$$

Where

$$H'^Z \left| \psi_8 \right\rangle = \frac{eB_{ext}}{2m} \left(\hat{L}_z + 2\hat{S}_z \right) \left(-\sqrt{\tfrac{2}{3}} \left| 1, -1 \right\rangle \left| \tfrac{1}{2}, \tfrac{1}{2} \right\rangle + \sqrt{\tfrac{1}{3}} \left| 1, 0 \right\rangle \left| \tfrac{1}{2}, -\tfrac{1}{2} \right\rangle \right)$$

$$= \frac{eB_{ext}}{2m} \left[\left(-\sqrt{\tfrac{2}{3}} \right)\left((-\hbar) + 2(\tfrac{1}{2}\hbar) \right) \left| 1, -1 \right\rangle \left| \tfrac{1}{2}, \tfrac{1}{2} \right\rangle + \left(-\sqrt{\tfrac{1}{3}} \right)\left((0) + 2(-\tfrac{1}{2}\hbar) \right) \left| 1, 0 \right\rangle \left| \tfrac{1}{2}, -\tfrac{1}{2} \right\rangle \right]$$

$$= \frac{eB_{ext}}{2m} \left[\left(-\sqrt{\tfrac{2}{3}} \right)(0) \left| 1, -1 \right\rangle \left| \tfrac{1}{2}, \tfrac{1}{2} \right\rangle + \left(\sqrt{\tfrac{1}{3}} \right)(-\hbar) \left| 1, 0 \right\rangle \left| \tfrac{1}{2}, -\tfrac{1}{2} \right\rangle \right]$$

$$= -\sqrt{\tfrac{1}{3}}\hbar \frac{eB_{ext}}{2m} \left| 1, 0 \right\rangle \left| \tfrac{1}{2}, -\tfrac{1}{2} \right\rangle$$

So,

$$W_{7,8}^{Z} = \langle \psi_7 | H'^{Z} | \psi_8 \rangle = \left(\sqrt{\tfrac{1}{3}} \langle 1,-1 | \langle \tfrac{1}{2}, \tfrac{1}{2} | + \sqrt{\tfrac{2}{3}} \langle 1,0 | \langle \tfrac{1}{2}, -\tfrac{1}{2} | \right) \left(-\sqrt{\tfrac{1}{3}} \hbar \frac{eB_{ext}}{2m} \right) |1,0\rangle |\tfrac{1}{2}, -\tfrac{1}{2}\rangle$$

$$W_{7,8}^{Z} = -\sqrt{\tfrac{1}{3}} \langle 1,-1 | \langle \tfrac{1}{2}, \tfrac{1}{2} | \sqrt{\tfrac{1}{3}} \hbar \frac{eB_{ext}}{2m} |1,0\rangle |\tfrac{1}{2}, -\tfrac{1}{2}\rangle - \sqrt{\tfrac{2}{3}} \langle 1,0 | \langle \tfrac{1}{2}, -\tfrac{1}{2} | \sqrt{\tfrac{1}{3}} \hbar \frac{eB_{ext}}{2m} |1,0\rangle |\tfrac{1}{2}, -\tfrac{1}{2}\rangle$$

$$W_{7,8}^{Z} = -\tfrac{1}{3} \hbar \frac{eB_{ext}}{2m} \underbrace{\langle 1,-1 | \langle \tfrac{1}{2}, \tfrac{1}{2} \| 1,0\rangle | \tfrac{1}{2}, -\tfrac{1}{2}\rangle}_{0} - \frac{\sqrt{2}}{3} \hbar \frac{eB_{ext}}{2m} \underbrace{\langle 1,0 | \langle \tfrac{1}{2}, -\tfrac{1}{2} \| 1,0\rangle | \tfrac{1}{2}, -\tfrac{1}{2}\rangle}_{1}$$

$$W_{7,8}^{Z} = -\frac{\sqrt{2}}{3} \hbar \frac{eB_{ext}}{2m}$$

As for

$$W_{7,8}^{fine} = \langle \psi_7 | H'^{fine} | \psi_8 \rangle$$

It's easiest to express the wavefunctions in terms of the j, m_j basis set since then it's easy to express the energies:

$$H'^{fine} | j, m_j \rangle = \frac{(E_o)^2}{2mc^2 n^4} \left(3 - \frac{4n}{j + \tfrac{1}{2}} \right) | j, m_j \rangle$$

$$H'^{fine} | \psi_8 \rangle = \frac{(E_2)^2}{2mc^2 2^4} \left(3 - \frac{4 \cdot 2}{\tfrac{1}{2} + \tfrac{1}{2}} \right) | \tfrac{1}{2}, -\tfrac{1}{2} \rangle = \frac{(E_o)^2}{2mc^2 16} (3 - 8) | \tfrac{1}{2}, -\tfrac{1}{2} \rangle = -\frac{(E_o)^2}{mc^2 32} 5 | \tfrac{1}{2}, -\tfrac{1}{2} \rangle$$

However, all this work is for nothing because

$$W_{7,8}^{fine} = \langle \tfrac{3}{2}, -\tfrac{1}{2} | - \frac{(E_o)^2}{mc^2 32} 5 | \tfrac{1}{2}, -\tfrac{1}{2} \rangle = -\frac{(E_o)^2}{mc^2 32} 5 \langle \tfrac{3}{2}, -\tfrac{1}{2} \| \tfrac{1}{2}, -\tfrac{1}{2} \rangle = 0$$

So,

$$W_{7,8} = W_{7,8}^{fine} + W_{7,8}^{Z} = 0 - \frac{\sqrt{2}}{3} \hbar \frac{eB_{ext}}{2m}$$

That's the $-W_{7,8}^{Z} = \frac{\sqrt{2}}{3} \beta$ that Griffiths has in the 7,8 (and the 8,7) location of the $-W$ matrix.

As for the energies, they'd be gotten from the 'characteristic equation'; however, since the matrix is diagonal for the first four states, it's easy to read the energies right off the diagonal.

$$E_3'^{(1)} = W_{3,3} = W_{3,3}^{Z} + W_{3,3}^{fine} = -(\gamma - 2\beta) = -\gamma + 2\beta$$

For the next two, this could be broken down into the a sub matrix, and you can find *it's* characteristic equation yields the two energy corrections.

6.5   Hyperfine Splitting (of ground state)

The spins of the quarks that make up the proton in the Hydrogen nucleus are responsible for producing a magnetic field with a "gyromagnetic ratio" $g_p = 5.59$,

$$\hat{\mu}_p = \frac{g_p e}{2m} \hat{S}_p \text{ from Griffiths' } \textit{other} \text{ text, } \vec{B}_p = \frac{1}{4\pi \varepsilon_o c^2 r^3} \left[3(\vec{\mu}_p \cdot \hat{r}) \hat{r} - \vec{\mu}_p \right] + \frac{2}{3 \varepsilon_o c^2} \vec{\mu}_p \delta^3(\vec{r})$$

So, the energy associated with the electron's spin interacting with the proton's spin is

$$E^{e,p} = -\vec{\mu}_e \cdot \vec{B}_p = -\frac{1}{4\pi \varepsilon_o c^2 r^3} \left[3(\vec{\mu}_p \cdot \hat{r})(\vec{\mu}_e \cdot \hat{r}) - \vec{\mu}_e \cdot \vec{\mu}_p \right] + \frac{2}{3 \varepsilon_o c^2} \vec{\mu}_e \cdot \vec{\mu}_p \delta^3(\vec{r})$$

In the ground state, the electron has spin but no orbit, $\hat{\mu}_{e_1} = \dfrac{-e}{m}\hat{S}$

So, the term in the Hamiltonian would be

$$\hat{H}_1^{e,p} = \frac{g_p e^2}{2m_e m_p}\left(\frac{1}{4\pi\varepsilon_o c^2 r^3}\left[3(\hat{S}_p \cdot \hat{r})(\hat{S}_e \cdot \hat{r}) - \hat{S}_e \cdot \hat{S}_p\right] + \frac{2}{3\varepsilon_o c^2}\hat{S}_e \cdot \hat{S}_p \delta^3(\vec{r})\right)$$

So,

$$E_1^{(1)e,p} = \left\langle \Psi_1 \middle| \hat{H}_1^{e,p} \middle| \Psi_1 \right\rangle$$

$$E_1^{(1)e,p} = \frac{g_p e^2}{2m_e m_p}\left\langle \Psi_1 \middle| \left(\frac{1}{4\pi\varepsilon_o c^2 r^3}\left[3(\hat{S}_p \cdot \hat{r})(\hat{S}_e \cdot \hat{r}) - \hat{S}_e \cdot \hat{S}_p\right] + \frac{2}{3\varepsilon_o c^2}\hat{S}_e \cdot \hat{S}_p \delta^3(\vec{r})\right) \middle| \Psi_1 \right\rangle$$

$$E_1^{(1)e,p} = \frac{g_p e^2}{2m_e m_p}\left(\frac{1}{4\pi\varepsilon_o c^2}\left\langle \Psi_1 \middle| \frac{\left[3(\hat{S}_p \cdot \hat{r})(\hat{S}_e \cdot \hat{r}) - \hat{S}_e \cdot \hat{S}_p\right]}{r^3} \middle| \Psi_1 \right\rangle + \frac{2}{3\varepsilon_o c^2}\left\langle \Psi_1 \middle| \hat{S}_e \cdot \hat{S}_p \delta^3(\vec{r}) \middle| \Psi_1 \right\rangle\right)$$

Now, since we're focusing on the ground state, we can get explicit about these inner products and the first term vanishes, leaving just

$$E_1^{(1)e,p} = \frac{g_p e^2}{3\varepsilon_o c^2 m_e m_p}\left\langle \Psi_1 \middle| \hat{S}_e \cdot \hat{S}_p \delta^3(\vec{r}) \middle| \Psi_1 \right\rangle$$

Where $\vec{S} \equiv \hat{S}_e + \hat{S}_p \Rightarrow S^2 = S_e^2 + S_p^2 + 2\hat{S}_e \cdot \hat{S}_p \Rightarrow \hat{S}_e \cdot \hat{S} = \frac{1}{2}\left(S^2 - S_e^2 - S_p^2\right)$

$$E_1^{(1)e,p} = \frac{g_p e^2}{6\varepsilon_o c^2 m_e m_p}\left\langle \Psi_1 \middle| \left(s(s+1)\hbar^2 - s_e(s_e+1)\hbar^2 - s_p(s_p+1)\hbar^2\right)\delta^3(\vec{r}) \middle| \Psi_1 \right\rangle$$

And since the electron and proton are both spin ½, that cleans up to

$$E_1^{(1)e,p} = \frac{g_p e^2\left(s(s+1) - \frac{3}{2}\right)\hbar^2}{6\varepsilon_o c^2 m_e m_p}\left\langle \Psi_1 \middle| \delta^3(\vec{r}) \middle| \Psi_1 \right\rangle = \frac{g_p e^2\left(s(s+1) - \frac{3}{2}\right)\hbar^2}{6\varepsilon_o c^2 m_e m_p}\left|\Psi_1(0)\right|^2 = \frac{g_p e^2\left(s(s+1) - \frac{3}{2}\right)\hbar^2}{6\varepsilon_o c^2 m_e m_p \pi a^3}$$

Now, this is a system of two spin-1/2 particles, so either the two spins aligned in one of the three triplet states, giving s = 1; or their anti-aligned giving s = 0.

$$\boxed{E_1^{(1)e,p} = \frac{g_p e^2 \hbar^2}{3\varepsilon_o c^2 m_e m_p \pi a^3}\begin{cases}\frac{1}{4} & \text{triplet} \\ -\frac{3}{4} & \text{singlet}\end{cases} = \Delta E\begin{cases}\frac{1}{4} & \text{triplet} \\ -\frac{3}{4} & \text{singlet}\end{cases}}$$

12.1 EPR paradox

Einstein, Podolsky, and Rosen's Position: Realists

Einstein, Podolsky, and Rosen's (and Bohm's) Experiment: Entangled Particles

$$\pi^o \to e^- + e^+$$

Since the pion was spinless, the electron and positron must, together, be described by the singlet state. In terms of any axis (though we often call it z):

$$|0,0\rangle = \tfrac{1}{\sqrt{2}}\left(\uparrow_- \downarrow_+ + \uparrow_+ \downarrow_-\right)$$

If you measure the spin projection of the electron, then you instantly know the spin projection of the positron, regardless of how far away it is. E, P, and R concluded that the spin projection must have existed all along, so Q.M. is an incomplete theory – it describes our incomplete knowledge of the system not the full reality of the system.

12.2 Bell's Theorem / Inequality for hidden-variables theories

In the abstract, call the additional pieces of information (that nature has but don't show up in Q.M) λ. Then the outcome of a spin measurement would be a function of this variable. For example, if you wanted to know the electron's spin projection along some axis a, that would be determined by the function

$$S_a^e = S^e(\hat{a},\lambda) = \pm \tfrac{\hbar}{2}.$$

Of course, since the positron's spin is the opposite, the function that yields its orientation must be

$$S^p(\hat{a},\lambda) = -S^e(\hat{a},\lambda)$$

Product of electron and positron spin measurements along the *same* axis

Since they are opposite, their product must always yield

$$- S^p(\hat{a},\lambda)S^p(\hat{a},\lambda) = -S_a^p S_a^P = -\left(\tfrac{\hbar}{2}\right)^2$$

Product of electron and positron spin measurements along *different* axes

$$\langle S_a^p S_b^e\rangle = -\int \rho(\lambda)S^p(\hat{a},\lambda)S^p(\hat{b},\lambda)d\lambda \ \ \text{or} \ \ \langle S_a^p S_c^e\rangle = -\int \rho(\lambda)S^p(\hat{a},\lambda)S^p(\hat{c},\lambda)d\lambda$$

Then $\langle S_a^p S_b^e\rangle - \langle S_a^p S_c^e\rangle = -\int \rho(\lambda)S^p(\hat{a},\lambda)\left(S^p(\hat{b},\lambda) - S^p(\hat{c},\lambda)\right)d\lambda$

Where $\rho(\lambda)$ is the probability density of this variable (look back at chapter 1 if this seems hazy).

$$1 = \int \rho(\lambda)d\lambda$$

so $\langle S_a^p S_b^e\rangle - \langle S_a^p S_c^e\rangle = -\int \rho(\lambda)S^p(\hat{a},\lambda)S^p(\hat{b},\lambda)\left(1 - \left(\tfrac{2}{\hbar}\right)^2 S^p(\hat{b},\lambda)S^p(\hat{c},\lambda)\right)d\lambda$

can rephrase as the inequality

$$\left|\langle S_a^p S_b^e\rangle - \langle S_a^p S_c^e\rangle\right| \le \int \rho(\lambda)\left(\tfrac{\hbar}{2}\right)^2\left(1 - \left(\tfrac{2}{\hbar}\right)^2 S^p(\hat{b},\lambda)S^p(\hat{c},\lambda)\right)d\lambda = \left(\tfrac{\hbar}{2}\right)^2\int \rho(\lambda)d\lambda - \int \rho(\lambda)S^p(b,\lambda)S^p(c,\lambda)d\lambda$$

$$\boxed{\left|\langle S_a^p S_b^e\rangle - \langle S_a^p S_c^e\rangle\right| \le \left(\tfrac{\hbar}{2}\right)^2 + \langle S_b^p S_c^e\rangle}$$

Quantum Mechanics' Prediction

Say you measure the positron's projection along the a axis to be $S^p_{-a} = -\frac{\hbar}{2}$, then you know the electron's projection along that axis is $S^e_a = \frac{\hbar}{2}$. But if you measure its projection along the b axis instead, you'd get $S^e_{+b} = +\frac{\hbar}{2}$ with probability $P^e_{+b} = \cos^2\left(\frac{\theta_{b-a}}{2}\right)$ or $S^e_{-b} = -\frac{\hbar}{2}$ with probability $P^e_{-b} = \sin^2\left(\frac{\theta_{b-a}}{2}\right)$.

So,

$$\left\langle S^p_a S^e_b \right\rangle = S^p_{-a} \cdot \left(P^e_{+b} S^e_{+b} + P^e_{-b} S^e_{-b} \right) = -\frac{\hbar}{2} \cdot \left(\frac{\hbar}{2} \cos^2\left(\frac{\theta_{b-a}}{2}\right) - \frac{\hbar}{2} \sin^2\left(\frac{\theta_{b-a}}{2}\right) \right) = -\left(\frac{\hbar}{2}\right)^2 \cos(\theta_{b-a}) = -\left(\frac{\hbar}{2}\right)^2 \hat{a} \cdot \hat{b}$$

Now, if you were instead to measure the positron to have the opposite alignment, the signs for each term would be flipped, and you'd get the same *product*, so we have the average product. Thus, Q.M. predicts that

$$\left| \left\langle S^p_a S^e_b \right\rangle - \left\langle S^p_a S^e_c \right\rangle \right| = \left| \left(-\left(\frac{\hbar}{2}\right)^2 \hat{a} \cdot \hat{b} \right) - \left(-\left(\frac{\hbar}{2}\right)^2 \hat{a} \cdot \hat{c} \right) \right| = \left(\frac{\hbar}{2}\right)^2 \left| \hat{a} \cdot \left(\hat{b} - \hat{c} \right) \right|$$

Quantum vs. Bell's

how does Quantum Mechanics predict the left and right-hand sides of Bell's inequality should be related?

$$\left| \left\langle S^p_a S^e_b \right\rangle - \left\langle S^p_a S^e_c \right\rangle \right| \ ? \ \left(\frac{\hbar}{2}\right)^2 + \left\langle S^p_b S^e_c \right\rangle$$

$$\left| \left(-\left(\frac{\hbar}{2}\right)^2 \hat{a} \cdot \hat{b} \right) - \left(-\left(\frac{\hbar}{2}\right)^2 \hat{a} \cdot \hat{c} \right) \right| \ ? \ \left(\left(\frac{\hbar}{2}\right)^2 - \left(\frac{\hbar}{2}\right)^2 \hat{b} \cdot \hat{c} \right)$$

$$\left(\frac{\hbar}{2}\right)^2 \left| \hat{a} \cdot \hat{b} - \hat{a} \cdot \hat{c} \right| \ ? \ \left(\frac{\hbar}{2}\right)^2 \left(1 - \hat{b} \cdot \hat{c} \right)$$

$$\left| \hat{a} \cdot \hat{b} - \hat{a} \cdot \hat{c} \right| \ ? \ \left(1 - \hat{b} \cdot \hat{c} \right)$$

Specific Case

For example, if $\hat{a} = \hat{z}$, $\hat{b} = \hat{x}$, and $\hat{c}$ is 45° up from x toward z. Then the inequality would claim

$$\frac{1}{\sqrt{2}} \leq \left(1 - \frac{1}{\sqrt{2}} \right) = \frac{\sqrt{2}-1}{\sqrt{2}}$$

$$2 \leq \sqrt{2}$$

Wrong!

And experiment backs up quantum mechanics – not Bell's inequality.

Interpretations

Be familiar with some of the major interpretations – how they handle Bell's Inequality, How they handle the Measurement Problem, and generally what some of their strengths / weaknesses are (of course, strengths and weaknesses are in the eye of the beholder).