Phys 3820, Fall 2010
Exam #1

1. A particle of mass m is trapped in a one–dimensional potential

$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 < x < a \\ \infty & x > a \end{cases}$$

i.e. the 1–D box. To this potential we add a "small" perturbation

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 \sin^2\left(\frac{\pi x}{a}\right) & 0 < x < a \\ 0 & x > a \end{cases}$$

a) For this to be a "small" perturbation as advertised, what should be true about V_0?

We would expect the maximum value of the perturbing potential energy to be small compared to the energy of ground state of the unperturbed system, namely $E_{\rm gs} = \frac{\pi^2\hbar^2}{2ma^2}$.

b) Find the first–order correction to the energy of the ground state. (If the integrals are too tedious, you don't need to finish them, but write them out *clearly*.

Evaluate $\langle\psi_{\rm gs}|H'|\psi_{\rm gs}\rangle$:

$$\begin{aligned} E_{\rm gs} &= \langle\psi_{\rm gs}|H'|\psi_{\rm gs}\rangle = \frac{2}{a}V_0\int_0^1 \sin\left(\frac{\pi x}{a}\right)\sin^2\left(\frac{\pi x}{a}\right)\sin\left(\frac{\pi x}{a}\right)\,dx \\ &= \frac{2V_0}{a}\int_0^a \sin^4\left(\frac{\pi x}{a}\right)\,dx = \frac{2V_0}{a}\left[\frac{3}{8}x - \frac{\sin(2\pi x/a)}{4\pi/a} + \frac{\sin(4\pi x/a)}{32\pi/a}\right]\Bigg|_0^a \\ &= \frac{6V_0}{8a}a = \frac{3V_0}{4} \end{aligned}$$

c) Set up some expressions to show how you would evaluate the first–order correction to the ground state wave function. (Go as far as you can with this; show me that you know how it is done.)

Here of course we must evaluate the sum

$$\psi_1^1(x) = \sum_{n\neq 1}\frac{\langle\psi_n|H'|\psi_1\rangle}{(E_1 - E_n)}\psi_n(x)$$

$$\begin{aligned} \langle\psi_n|H'|\psi_1\rangle &= \frac{2V_0}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\sin^2\left(\frac{\pi x}{a}\right)\sin\left(\frac{\pi x}{a}\right)\,dx \\ &= \frac{2V_0}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\sin^3\left(\frac{\pi x}{a}\right)\,dx \end{aligned}$$

This will be zero for even n. In fact it is zero for *all* n excpet for $n = 3$ and for that we get

$$\langle \psi_n | H' | \psi_1 \rangle = \frac{2V_0}{a}\left(-\frac{a}{8}\right) = -\frac{V_0}{4}$$

Using

$$E_1 - E_3 = (1-9)\frac{\pi^2\hbar^2}{2ma^2} = -\frac{4\pi^2\hbar^2}{ma^2}$$

which gives

$$\psi_1^1(x) = -\frac{ma^2}{4\pi^2\hbar^2}(-V_0/4)\psi_3(x) = \frac{V_0 ma^2}{16\pi^2\hbar^2}\psi_3(x)$$

2. a) The poor man's relativistic correction to the Schrödinger Hamiltonian,

$$H'_{\rm rel} = -\frac{p^4}{8m^3c^2} \qquad ,$$

was used for the H atom and also for the harmonic oscillator in a homework problem.

Say a few words about why this is only a *crude* fix-up for relativity. (Are there better ways?)

This term came about from a first-order approximation to the non-quantum kinetic energy expression in terms of momentum. We simply substituted the *operator* for p^2 in place of the *number* for p^2.

Though this procedure is probably correct to lowest order it is a clumsy way to avoid taking the square root of an *operator*. In fact there are good *relativistic* equations for wave functions of which the Dirac equation is the proper one for electrons. It was successful in predicting the spin properties of the electron and its anti-particles, namely positrons.

b) *Explain* (in words, mostly) the origin of the spin-orbit term

$$H'_{\rm so} = \left(\frac{e^2}{8\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\mathbf{L}\cdot\mathbf{S}$$

The physical origin of this term is that in the frame of the "orbiting" electron one observes a magnetic field from the orbiting proton. The magnetic moment of the electron interacts with this field to give an energy dependence on the spin. We did a crude derivation of the observed magnetic field, which gave the $\mathbf{L}$ dependence and found the value of the operator $\mathbf{B}\cdot\boldsymbol{\mu}_e$.

With such a crude derivation we were not surprised to learn that in a more careful treatment some factors of 2 had to be added.

3. a) Explain what is the basic problem with naively applying the formula

$$E_i^1 = \langle \psi_i^0 | H' | \psi_i^0 \rangle$$

when ψ_i^0 is a member of a set of degenerate states.

Before "applying" the perturbation (i.e. with only H_0) we are free to choose any linear combination of the degenerate states and they are still proper energy eigenstates. That is not true after the perturbation is applied, as only specific linear combinations will become the perturbed states with their individual values of E_i^1. Naive use of the formula is wrong because it does not start with the proper unperturbed states.

b) In solving for the first-order energy perturbations of a set of degenerate states you construct the W matrix. What do the eigenvectors of the W matrix represent?

They are the "proper" linear combinations of the original states (as mentioned in (a)) which correspond to a system with a vanishing value of the perturbation Hamiltonian H'.

4. When we chose states that were "good" for the perturbation $H'_{\rm so}$, we needed eigenstates of $\mathbf{L}\cdot\mathbf{S}$; these were states of "good" j, l (and $s = \frac{1}{2}$). Show that the eigenvalues of the operator $\mathbf{L}\cdot\mathbf{S}$ are

$$\frac{\hbar^2}{2}[j(j+1) - l(l+1) - \tfrac{3}{4}]$$

Since $\mathbf{J} = \mathbf{L} + \mathbf{S}$, then the operator $\mathbf{J}^2$ is given by:

$$\mathbf{J}^2 = (\mathbf{L}+\mathbf{S})^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L}\cdot\mathbf{S}$$

so

$$\mathbf{L}\cdot\mathbf{S} = \tfrac{1}{2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2)$$

When operating on a state which is an eigen state of $\mathbf{J}^2$, $\mathbf{L}^2$ and $\mathbf{S}^2$ (but *not* of m_l or m_s) then $\mathbf{J}^2$ gives $\hbar^2 j(j+1)$ etc. for L and S. So for these states we can replace:

$$\mathbf{L}\cdot\mathbf{S} = \frac{\hbar^2}{2}(j(j+1) - l(l+1) - s(s+1))$$

Though j and l can take on different values for the H-atom states, s is always $\frac{1}{2}$. Thus:

$$\mathbf{L}\cdot\mathbf{S} = \frac{\hbar^2}{2}(j(j+1) - l(l+1) - \tfrac{3}{4})$$

5. It was discussed in class that the corrections of QED (which we did not calculate) are in fact bigger than that of the hyper-fine interaction, which we *did* do.

In a paragraph, describe what the QED correction is all about.

The theory of QED gives the proper treatment of the EM field for the dynamics of electrons. Basically it considers the possibility that photons are emitted by the electrons interacting with other charges and then re-absorbed. It also allows for the possibility that a photon can become a virtual electron-positron pair.

6. It can be shown that the effect of "vacuum polarization" in QED is to replace the potential of the proton (in MKS units) by

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} - \frac{\alpha}{15\pi\epsilon_0}\frac{e^2}{m^2}\delta^3(\mathbf{r})$$

What is the effect of vacuum polarization on the ground state energy of the H atom?

I goofed somewhat in giving this because it was taken from a book which used "units" with $\hbar = c = 1$, something we may not be ready for, yet. To get the units right one needs to replace them to get an expression in units of energy and this is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} - \frac{\alpha}{15\pi\epsilon_0 \hbar c}\frac{e^2(\hbar c)^3}{(m^2c^4)}\delta^3(\mathbf{r})$$

Anyway, allowing for that, the perturbation to the Hamiltonian is

$$H' = -\frac{\alpha e^2(\hbar c)^2}{15\pi\epsilon_0(m^2c^4)}\delta(\mathbf{r})$$

and the important thing is that it is a delta-function term and gives a shift in energy of the 1s state of

$$E^1_{\rm gs} = \langle\psi_{100}|H'|\psi_{100}\rangle = -\frac{\alpha e^2(\hbar c)^2}{15\pi\epsilon_0(m^2c^4)}\int |\psi_{100}|^2\delta(\mathbf{r})\,d^3r$$

Since

$$\psi_{100}(\mathbf{0}) = \frac{1}{\sqrt{\pi a^3}}$$

this gives

$$E^1_{\rm gs} = -\frac{\alpha e^2(\hbar c)^2}{15\pi\epsilon_0(m^2c^4)}\frac{1}{\pi a^3}$$

7. For the weak-field Zeeman effect, how is the $l = 2$, $j = \frac{3}{2}$ state affected? (Into how many levels is it split?) give an expression for the first-order corrections to the energy for an external field of strength $B_{\rm ext}$.

Here, with $j = \frac{3}{2}$ and $L = 2$ the Landé g-factor is

$$\begin{aligned} g_J &= 1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)} = 1 + \frac{\frac{15}{4} - 6 + \frac{3}{4}}{2\cdot\frac{15}{4}} \\ &= 1 - \frac{\frac{6}{4}}{\frac{15}{2}} = 1 - \frac{12}{60} = \frac{4}{5} \end{aligned}$$

Then the first-order energies of the states are given by

$$E^1_Z = \mu_B g_J m_j B_{\rm ext} = \frac{4}{5}\mu_B m_j B_{\rm ext}$$

for $m = \frac{-3}{2}, \ldots, +\frac{3}{2}$.

8. A somewhat open–ended problem:

Consider the spherical square well, given in spherical coordinates by

$$V(r) = \begin{cases} -V_0 & r < a \\ 0 & r > a \end{cases}$$

Though this problem can be solved "exactly" (in the sense that the functions are well–known) one might try to find a variational solution.

Think of a trial function with an adjustable parameter which might work, and outline the steps you would take to get an upper limit on the ground state energy.

A sensible choice for the trial wave function would be a hydrogenic function with an adjustable parameter in the exponent:

$$\psi(\mathbf{r}) = Ae^{-br}$$

First, normalize the wave function (old stuff):

$$1 = \int |\psi|^2 \, d^3\mathbf{r} = 4\pi A^2 \int_0^\infty r^2 e^{-2br} \, dr = 4\pi A^2 \cdot 2 \left(\frac{1}{2b}\right)^3 = \frac{\pi}{b^3}$$

which gives

$$A = \sqrt{\frac{b^3}{\pi}}$$

Find $\langle V \rangle$:

$$\begin{aligned}
\langle V \rangle &= \int V(r)|\psi|^2 \, d^3\mathbf{r} = 4\pi \frac{b^3}{\pi}(-V_0) \int_0^a r^2 e^{-2br} \\
&= (-4V_0 b^3)\left(-\frac{1}{4b^3}\right)\left(-1 + (1 + ba + 2a^2b^2)e^{-2ba}\right) \\
&= -V_0 - V_0(1 + ba + 2a^2b^2)e^{-2ba}
\end{aligned}$$

Find $\langle T \rangle$:

$$\begin{aligned}
T\psi(r) &= -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right)\right] \\
&= -\frac{\hbar^2 A}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(-br^2 e^{-br}\right)\right] \\
&= -\frac{\hbar^2 A}{2m}\frac{1}{r^2}(-2br + b^2r^2)e^{-br} = -\frac{\hbar^2 A}{2m}\left(\frac{-2b}{r} + b^2\right)e^{-br}
\end{aligned}$$

Then $\langle T \rangle$ is

$$\begin{aligned}
\langle T \rangle &= -\frac{\hbar^2}{2m}\frac{b^3}{\pi}(4\pi)\int_0^\infty (-2br + b^2r^2)e^{-2br} \, dr \\
&= -\frac{2\hbar^2 b^3}{m}\left[-2b\left(\frac{1}{2b}\right)^2 + b^2 2\left(\frac{1}{2b}\right)^3\right] \\
&= -\frac{2\hbar^2 b^3}{m}\left[-\frac{1}{2b} + \frac{1}{4b}\right] = -\frac{2\hbar^2 b^3}{m} \cdot \left(-\frac{1}{4b}\right) = +\frac{\hbar^2 b^2}{2m}
\end{aligned}$$

The expression for $\langle H\rangle$ is now

$$\langle H\rangle = \frac{\hbar^2 b^2}{2m} - V_0 - V_0(1 + ba + 2a^2b^2)e^{-2ba}$$

This indeed is an expression that would require numerics to minimize. I will leave it here.

9. The Born–Oppenheimer approximation is essential in the treatment of molecules. What is it? Why is it sensible? Why is it so useful?

It is the approximation that the nuclei in the molecule are nailed down at fixed coordinate while we solve for the electron motion. This gives electornic energies with the nuclear separations as parameters. Later we can solve an *effective* Schrödinger equation for the motion of the nuclei.

It is sensible becuase the nuclei are so much more massive than the electrons that we expect (with our physical horse-sense) that the electrons rapidly adjust to changes in positions of the nuclei.

It's useful because it makes it lowers the number of degrees of freedom (coordinates) in the problem making one that is nearly impossible to one that is merely difficult!

10. In the famous Problem 7.20, how was it proven that a particle can become "trapped" at the intersection of the quantum wires?

In this problem there are intersecting channels where the potential energy V is zero (and infinite outside). There is a continuum of states with energy greater than the threshold energy; all of these states are non-normalizeable states corresponding to free motion in the channel (i.e. one of its branches). We will have a bound state if we have a localized wave function with an energy eigenvalue *less than* this continuum threshold.

In this messy problem, Griffiths suggests a trial wave function which behaves like we think a localized state should, with an adjustable parameter. After much math and algebra (which is rather messy because the trial wave function does not have continuous slopes) we find that the upper bound on the energy is about 0.88 of the threshold so the true ground state must have an energy lower than that and hence is a bound state.

The problem can solved "exactly" on a computer and it is found that the exact energy eigenvalue is 0.66 of the threshold value, much lower. So here the variational principle was only good for showing its *existence*.

Useful Equations

Math

$$\int_0^\infty x^n e^{-x/a} = n!\, a^{n+1}$$

$$\int_0^\infty x^{2n} e^{-x^2/a^2}\, dx = \sqrt{\pi}\frac{(2n)!}{n!}\left(\frac{a}{2}\right)^{2n+1} \qquad \int_0^\infty x^{2n+1} e^{-x^2/a^2}\, dx = \frac{n!}{2} a^{2n+2}$$

$$\int_a^b f\,\frac{dg}{dx}\,dx = -\int_a^b \frac{df}{dx}\,g\,dx + fg\bigg|_a^b$$

Numbers

$$\hbar = 1.05457 \times 10^{-34}\ \mathrm{J\cdot s} \qquad m_{\mathrm{e}} = 9.10938 \times 10^{-31}\ \mathrm{kg} \qquad m_{\mathrm{p}} = 1.67262 \times 10^{-27}\ \mathrm{kg}$$

$$e = 1.60218 \times 10^{-19}\ \mathrm{C} \qquad c = 2.99792 \times 10^{8}\ \mathrm{\tfrac{m}{s}}$$

Physics

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi \qquad P_{ab} = \int_a^b |\Psi(x,t)|^2\,dx \qquad p \to \frac{\hbar}{i}\frac{d}{dx}$$

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2\,dx = 1 \qquad \langle x\rangle = \int_{-\infty}^{\infty} x|\Psi(x,t)|^2\,dx \qquad \langle p\rangle = \int_{-\infty}^{\infty} \Psi^*\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi\,dx$$

$$\sigma = \sqrt{\langle j^2\rangle - \langle j\rangle^2} \qquad \sigma_x\sigma_p \geq \frac{\hbar}{2}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi \qquad \phi(t) = e^{-iEt/\hbar} \qquad \Psi(x,t) = \sum_{n=1}^{\infty} c_n\psi_n(x)e^{-iE_nt/\hbar} = \sum_{n=1}^{\infty}\Psi_n(x,t)$$

$$\infty \text{ Square Well:} \qquad E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \qquad \psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)$$

$$\int \psi_m(x)^*\psi_n(x)\,dx = \delta_{mn} \qquad c_n = \int \psi_n(x)^*\,f(x)\,dx \qquad \sum_{n=1}^{\infty}|c_n|^2 = 1 \qquad \langle H\rangle = \sum_{n=1}^{\infty}|c_n|^2E_n$$

$$\text{Harmonic Oscillator:} \qquad V(x) = \tfrac{1}{2}m\omega^2x^2 \qquad \frac{1}{2m}[p^2 + (m\omega x)^2]\psi = E\psi$$

$$a_\pm \equiv \frac{1}{\sqrt{2\hbar m\omega}}(\mp ip + m\omega x) \qquad [A,B] = AB - BA \qquad [x,p] = i\hbar$$

$$H(a_+\psi) = (E+\hbar\omega)(a_+\psi) \qquad H(a_-\psi) = (E-\hbar\omega)(a_+\psi) \qquad a_-\psi_0 = 0$$

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2} \qquad \psi_1(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\sqrt{\frac{2m\omega}{\hbar}}\,xe^{-\frac{m\omega}{2\hbar}x^2}$$

$$\text{Free particle:} \qquad \Psi_k(x) = Ae^{i(kx - \frac{\hbar k^2}{2m})t} \qquad v_{\mathrm{phase}} = \frac{\omega}{k} \qquad v_{\mathrm{group}} = \frac{d\omega}{dk}$$

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i(kx - \frac{\hbar k^2}{2m}t)}\, dk \qquad \phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-ikx}\, dx$$

Delta Fn Potl: $\psi(x) = \frac{\sqrt{m\alpha}}{\hbar} e^{-m\alpha|x|/\hbar^2}$ $\qquad E = -\frac{m\alpha^2}{2\hbar^2}$

$$f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} \exp(ipx/\hbar) \qquad [\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} = \hat{B}\hat{A} \qquad \Phi(p,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ipx/\hbar} \Psi(x,t)\, dx$$

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2 \qquad \sigma_x \sigma_p \geq \frac{\hbar}{2} \qquad \Delta E \Delta t \geq \frac{\hbar}{2}$$

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] + V(r)\psi = E\psi$$

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi) \qquad \frac{d^2\Phi}{d\phi^2} = -m^2\Phi \qquad \sin\theta \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + [\ell(\ell+1)\sin^2\theta - m^2]\Theta = 0$$

$$Y_0^0 = \sqrt{\frac{1}{4\pi}} \qquad Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta \qquad Y_1^{\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi}$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1) \qquad Y_2^{\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin\theta\, \cos\theta e^{\pm i\phi} \qquad Y_2^{\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta\, e^{\pm 2i\phi} \text{etc.}$$

$$u(r) \equiv rR(r) \qquad -\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu$$

$$a = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10} \text{ m} \qquad E_n = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} \equiv \frac{E_1}{n^2} \qquad \text{for} \quad n = 1, 2, 3, \ldots$$

where $E_1 = -13.6$ eV.

$$R_{10}(r) = 2a^{-3/2} e^{-r/a} \qquad R_{20}(r) = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{1}{2} \frac{r}{a} \right) e^{-r/2a} \qquad R_{21}(r) \frac{1}{\sqrt{24}} a^{-3/2}\, \frac{r}{a}\, e^{-r/2a}$$

$$\lambda f = c \qquad E_\gamma = hf \qquad \frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \qquad \text{where} \qquad R = \frac{m}{4\pi c \hbar^3} \left(\frac{c^2}{4\pi\epsilon_0} \right)^2 = 1.097 \times 10^7 \text{ m}^{-1}$$

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \qquad [L_x, L_y] = i\hbar L_z \qquad [L_y, L_z] = i\hbar L_x \qquad [L_z, L_x] = i\hbar L_y$$

$$L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \qquad L_\pm = \pm \hbar e^{\pm i\phi} \left(\frac{\partial}{\partial \theta} \pm i \cot\theta \frac{\partial}{\partial \phi} \right) \qquad L^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right]$$

$$L^2 f_l^m = \hbar^2 l(l+1) f_l^m \qquad L_z f_l^m = \hbar m f_l^m$$

$$[S_x, S_y] = i\hbar S_z \qquad [S_y, S_z] = i\hbar S_x \qquad [S_z, S_x] = i\hbar S_y$$

$$S^2|s\ m\rangle = \hbar^2 s(s{+}1)|s\ m\rangle \qquad S_z|s\ m\rangle = \hbar m|s\ m\rangle \qquad S_\pm|s\ m\rangle = \hbar\sqrt{s(s+1)-m(m\pm 1)}\,|s\ m{\pm}1\rangle$$

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_- \quad \text{where} \quad \chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\mathsf{S}^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \mathsf{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\mathsf{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \mathsf{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \mathsf{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\chi_+^{(x)} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad \chi_-^{(x)} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \qquad \chi_+^{(y)} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix} \qquad \chi_-^{(y)} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}$$

$$\mathbf{B} = B_0\mathbf{k} \qquad H = -\gamma B_0 \mathsf{S}_z \qquad E_+ = -(\gamma B_0\hbar)/2 \qquad E_- = +(\gamma B_0\hbar)/2$$

$$\chi(t) = a\chi_+ e^{-iE_+t/\hbar} + b\chi_- e^{-iE_-t/\hbar} = \begin{pmatrix} ae^{-iE_+t/\hbar} \\ be^{-iE_-t/\hbar} \end{pmatrix}$$

$$-\frac{\hbar^2}{2M}\nabla_R^2\psi - \frac{\hbar^2}{2\mu}\nabla_r^2\psi + V(\mathbf{r})\psi = E\psi \qquad \psi(\mathbf{r}_1, \mathbf{r}_2) = \pm\psi(\mathbf{r}_2, \mathbf{r}_1)$$

$$E_n^1 = \langle\psi_n^0|H'|\psi_n^0\rangle \qquad \psi_n^1 = \sum_{m\neq n}\frac{\langle\psi_m^0|H'|\psi_n^0\rangle}{(E_n^0 - E_m^0)}\psi_m^0 \qquad E_n^2 = \sum_{m\neq n}\frac{|\langle\psi_m^0|H'|\psi_n^0\rangle|^2}{E_n^0 - E_m^0} \qquad W_{ij} \equiv \langle i|H'|j\rangle$$

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \qquad H'_{\text{rel}} = -\frac{p^4}{8m^3c^2} \qquad H = -\mu\cdot\mathbf{B} \qquad \mathbf{B} = \frac{1}{4\pi\epsilon_0}\frac{e}{mc^2r^3}\mathbf{L} \qquad H'_{\text{so}} = \left(\frac{e^2}{8\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\mathbf{L}\cdot\mathbf{S}$$

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \qquad E^1_{\text{fs}} = \frac{(E_n)^2}{2mc^2}\left(3 - \frac{4n}{j+\frac{1}{2}}\right) \qquad E_{nj} = -\frac{13.6\ \text{eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right]$$

$$g_J = 1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)} \qquad E_Z^1 = \mu_B g_J B_{\text{ext}} m_j \qquad \mu_B \equiv \frac{e\hbar}{2m} = 5.788\times 10^{-5}\ \text{eV/T}$$

$$\boldsymbol{\mu}_p = \frac{g_p e}{2m_p}\mathbf{S}_p \qquad \boldsymbol{\mu}_e = -\frac{e}{m_e}\mathbf{S}_e \qquad E^1_{\text{hf}} = \frac{\mu_0 g_p e^2}{3\pi m_p m_e a^3}\langle\mathbf{S}_p\cdot\mathbf{S}_e\rangle = \frac{4g_p\hbar^4}{3m_p m_e^2 c^2 a^4}\begin{cases} +1/4 & \text{(triplet)} \\ -3/4 & \text{(singlet)} \end{cases}$$

$$E_{\text{gs}} \leq \langle\psi|H|\psi\rangle \equiv \langle H\rangle \qquad \psi_{1s}(\mathbf{r}) = \frac{1}{\sqrt{\pi a^3}}e^{-r/a}$$