**Phys 3820, Fall 2012**
**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

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 x & 0 < x < a/2 \\ V_0(a-x) & a/2 < x < a \\ 0 & a < x \end{cases}$$

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

We would expect the maximum value of this potential, $V_0 a/2$, to be much smaller than the ground state energy $\frac{\pi^2\hbar^2}{2ma^2}$.

**b)** Find the first–order correction to the energy of the ground state.

This is $\langle\psi_1|H'|\psi_1\rangle$, with $\psi_1(x) = \sqrt{2/a}\sin(\pi x/a)$:

$$\begin{aligned} E^1 &= \langle\psi_1|H'|\psi_1\rangle \\ &= V_0 \int_0^{a/2} \frac{2}{a}\sin^2\left(\frac{\pi x}{a}\right) x\, dx + V_0 \int_0^{a/2} \frac{2}{a}\sin^2\left(\frac{\pi x}{a}\right)(a-x)\, dx \\ &= V_0\sqrt{\frac{2}{a}}\left(\frac{1}{16}\frac{a^2}{\pi^2}(4+\pi^2) + \frac{1}{16}\frac{a^2}{\pi^2}(4+\pi^2)\right) \\ &= \frac{V_0 a}{4\pi^2}(4+\pi^2) \end{aligned}$$

**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; at least show me that you know how it is done.)

The first-order correction to the ground state wave function is

$$\psi^1_{gs} = \sum_{m\neq n} \frac{\langle\psi^0_m|H'|\psi^0_{gs}\rangle}{(E^2_{gs} - E^0_m)}\psi^0_m(x)$$

so that we need to compute

$$\langle\psi^0_m|H'|\psi^0_{gs}\rangle = \frac{2V_0}{a}\int_0^{a/2} x\sin\left(\frac{m\pi x}{a}\right)\sin\left(\frac{\pi x}{a}\right)\, dx + \frac{2V_0}{a}\int_{a/2}^{a}(a-x)\sin\left(\frac{m\pi x}{a}\right)\sin\left(\frac{\pi x}{a}\right)\, dx$$

while in the denominators we will use

$$E_{gs}^2 - E_m^0 = \frac{\pi^2\hbar^2}{2ma^2}(1-m^2)$$

That's as far as I'll take it, except to note that from symmetry about $a/2$, unless $m$ is odd we don't get a contribution.

**2.** The second-order correction to the energy of the ground state of a quantum system is always negative. Explain why.

The expression for the 2nd order correction to the ground state (denoted state $0$; assume non-degerate perturbation theory is OK here) is

$$E^2 = \sum_{m\neq 0} \frac{|\langle\psi_m|H'|\psi_n\rangle|^2}{(E_0 - E_m)}$$

is necessarily negative because the numerators are all positive and the denominators are negative since $E_m > E_0$.

**3. a)** The poor man's relativistic correction to the Schrödinger Hamiltonian that we used was

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

which was applied to the H atom and also for the harmonic oscillator in a homework problem.

Summarize how we arrived at this correction term and say a few words about why this is only a *crude* fix-up for relativity. (Are there better ways?)

The fix that we did was crude because we assumed that we could take an expansion of the square root of $numerical$ quantities (i.e. involving momentum $p$), substitute operators for them and use the same powers of the $operators$. This is questionable math at best but it would be crazy not to think that it must give something like the right answers.

There certainly are better ways to put relativity into quantum mechanics! The Dirac equation is the proper way to write a wave equation for an electron; it predicts spin and anti-particles. Relativistic QM is then superceded by the more complete theory of QED.

**4. a)** *Explain* (in words, mostly) the physical origin of the spin-orbit term

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

Be sure you spell out *why* the factors of $\mathbf{L}$ and $\mathbf{S}$ are there.

It can understood in terms satisfactory "for the scope of this course" as the interaction that the electron "feels" between its magnetic moment and the magnetic field generated by the proton which orbits the electron as seen in the electron's reference frame. The magnetic field made by the proton is proportional to operator $\mathbf{L}$ and the magnetic moment is proportional to the operator $\mathbf{S}$. The

Hamiltonian we use is the operator $H' = -\boldsymbol{\mu}\cdot\mathbf{B}$ with the substitutions indicated, making the result proportional to $\mathbf{L}\cdot\mathbf{S}$. Naive assumptions are corrected by various factors of 2 pending a rigorous derivation.

**b)** Explain what we meant by a "weak" external magnetic field imposed on the H atom and why for the perturbation arising from the field we must deal with states of "good $j$".

As the electron already "feels" a field from the proton from the orbital motion the external field imposed by scientists needs to be a lot weaker than this in order for it to be an even smaller perturbation on top of the spin-orbit effect. We found that a field much weaker than a few Tesla will be suitably "weak".

**c)** 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

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

From the relation $\mathbf{J} = \mathbf{L} + \mathbf{S}$ we get

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

so that the *action* of $\mathbf{L}\cdot\mathbf{S}$ when acting on eigenstates of $\mathbf{J}^2$, $\mathbf{L}^2$ and $\mathbf{S}^2$ is (substitute $\mathbf{J}^2 = \hbar^2 j(j+1)$, etc.)

$$\begin{aligned}\mathbf{L}\cdot\mathbf{S} &= \tfrac{1}{2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2) \\ &= \tfrac{1}{2}\hbar^2(j(j+1) - l(l+1) - \tfrac{1}{2}(\tfrac{1}{2}+1)) = \hbar^2/2\left[j(j+1) - l(l+1) - \tfrac{3}{4}\right]\end{aligned}$$

**5.** For the $n = 3$ states of the H atom (for which $l = 0, 1, 2$) in a weak magnetic field, describe what multiplets of states result from imposing the (weak) magnetic field) (A quantitative graph is not needed.)

With angular momentum addition, we will get three possible values of j, namely

$$j = \tfrac{1}{2}, \tfrac{3}{2}, \tfrac{5}{2}$$

but the Landé $g$ factor depends on both $j$ and $l$ so we get the values for $g_J$ corresponding to

$$l = 0,\ j = \tfrac{1}{2} \quad l = 1,\ j = \tfrac{1}{2} \quad l = 1,\ j = \tfrac{3}{2} \quad l = 2,\ j = \tfrac{3}{2} \quad l = 2,\ j = \tfrac{5}{2}$$

So the applied magnetic field produces 5 multiplets.

**6.** We didn't do it in class, so let's do it here! Or at leat as much as time allows.
Consider an H atom placed in a uniform electric field $\mathbf{E} = E_0\hat{\mathbf{k}}$ so that

$$H' = eE_0 z = eE_0 r\cos\theta$$

**a)** Will the ground state be affected by this perturbation (to first order)?
Well, it won't be, but explain why not.

Averaging $H'$ over the ground state to get $E^1$ gives

$$\langle \psi_{gs}|H'|\psi_{gs}\rangle = \frac{1}{\pi a^3}\int e^{-2r/a} eE_0 r\cos\theta\, d^3r$$

which will give zero from the integral of the cosine function (which is odd about $\theta = \pi/2$).

**b)** The first excited state(s) $(n = 2)$ *will* be affected by this perturbation. While the math will be a little long to work out in detail, describe how you would set things up to calculate the energy perturbation(s) to the $n = 2$ states.

While it is still true that symmetry will give zero for the integral

$$eE_0 \int |\psi_m(\mathbf{r})|^2 r\cos\theta\, d^3r$$

the excited state of the H atom has a degeneracy of 4 and one needs to use degenerate perturbation; the integral given above is just the diagonal element of the matrix $W$ which needs to be constructed. Its elements are proportional to

$$W_{ij} = \langle \psi_{2l'm'}|r\cos\theta|\psi_{2lm}\rangle$$

with 4 choices for $lm$. We note that since $\cos\theta$ is proportional to $Y_1^0$ we really want the matrix elements (angular integrals)

$$\langle Y_{l'}^{m'}|Y_1^0|Y_l^m\rangle$$

We can tell which of these are zero from considering:

| | |
|---|---|
| $Y_0^0$ | Even in $z$, Even in $x, y$ |
| $Y_1^0$ | Odd in $z$, Even in $x, y$ |
| $Y_l^{\pm 1}$ | Even in $z$, Odd in $x, y$ |

The result is that the only non-zero elements are when $lm = 00$ and $l'm' = 10$ and vice-versa.

One would then solve for the eigenvalues of $W$. It will turn out that there are only three roots so the $n = 2$ states split into three with the pertubed states formed from combinations of the original $2s$ and $2p_z$ wave functions.

**7.** Hey, do you know what else we left out of the Hamiltonian of the H atom?

**Gravity!**

In case you don't remember, the gravitational potential energy of two masses $m_1$ and $m_2$ separated by $r$ is

$$V_{\text{grav}} = -G\frac{m_1 m_2}{r}$$

Now you're probably thinking that it's pretty small, but figure out the first-order change in the ground state energy of H resulting from the gravitational interaction.

With $H' = -\frac{Gm_pm_e}{r}$, the first-order correction to the ground state energy is

$$\begin{aligned} E^1_{gs} &= \langle\psi_{gs}|H'|\psi_{gs}\rangle = -(Gm_pm_e)\frac{1}{\pi a^3}(4\pi)\int_0^\infty \frac{1}{r}e^{-2r/a}\,r^2\,dr \\ &= -\frac{4Gm_pm_e}{a^3}\int_0^\infty re^{-2r/a}\,dr = -\frac{4Gm_pm_e}{a^3}(a/2)^2 \\ &= -\frac{Gm_pm_e}{a} \end{aligned}$$

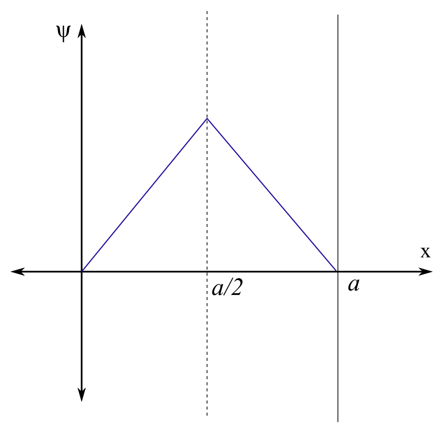
Plug in some numbers and get

$$E^1_{gs} = -(6.67\times10^{-11}\,\tfrac{\mathrm{N\cdot m^2}}{\mathrm{kg^2}})\frac{(1.67\times10^{-27}\ \mathrm{kg})(9.11\times10^{-31}\ \mathrm{kg})}{(0.529\times10^{-10}\ \mathrm{m})} = 1.9\times10^{-57}\ \mathrm{J} = 1.2\times10^{-38}\ \mathrm{eV}$$

Yes, it's unimaginably small, but that's how we would do the calculation.

**8.** In an example in the text Griffiths considers a trial function for the 1D box like the one shown here; essentially, two connected line segments.

We remarked that such a function requires special care in applying the variational principle. What special care is needed?




While the kinetic energy operator $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ gives zero on the straight parts of the curve, it is really undefined at $x = a/2$. There, the slope has a jump and we need to go back to the Schrödinger to evaluate the average value of the $d^2/dx^2$ operator properly; essentially the second derivative there is a delta function.

**9.** What is the cause of the (famous) $21-\mathrm{cm}$ "line" of hydrogen, a form of radiation which can be measured all through the universe?

The radiation of this wavelength arises from a transition between the two "hyperfine structure" states of the H atom; these are the two states that arise from the 1s state of the simple theory perturbed by the interaction of the proton and electron spins.

**10.** Consider the one-dimensional "box" potential

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

but suppose we had no clue how to solve it.

We consider the wave function for $0 \leq x \leq a$,

$$\psi(x) = Ax^2(a-x)^2$$

**a)** Find $A$

Well, this is tedious and if your calculator was able to do it, fine. I'll just show what Maple gave me. The trial wave function has to be normalized hence

$$\int_0^a [\psi(x)]^2\,dx = 1 = A^2\int_0^a x^4(a-x)^4\,dx = A^2\frac{630}{a^9}$$

Then

$$A = \left(\frac{630}{a^9}\right)^{1/2}$$

**b)** What upper bound does this trial function give on the ground state energy? (As usual get as far as you can with the math.)

We need to evaluate the expectation value of $H = T = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$. Evaluate

$$\begin{aligned}\frac{d^2}{dx^2}\psi(x) &= A\frac{d^2}{dx^2}x^2(a-x)^2 = A\frac{d^2}{dx^2}(a^2x^2 - 2ax^3 + x^4)\\ &= A(2a^2 - 12ax + 12x^2)\end{aligned}$$

This gives

$$\begin{aligned}\int \psi(x)H\psi(x)\,dx &= -A^2\frac{\hbar^2}{2m}\int_0^a x^2(a-x)^2(2a^2 - 12ax + 12x^2)\\ &= +\frac{630}{a^9}\frac{\hbar^2}{2m}\frac{2}{105} = \frac{\hbar^2}{2ma^2}(12)\end{aligned}$$

So we get the upper bound

$$E_{gs} \leq \frac{\hbar^2}{2ma^2}(12)$$

The exact answer is

$$E_{gs} = \frac{\hbar^2}{2ma^2}\pi^2$$

and it is lower because $\pi^2 \leq 12$.

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

The Born Oppenheimer approximation takes the impossible problem of solving for the quantum states of molecules and makes them merely difficult. In this approximation (to lowest order) the nuclei of the molecule are treated as being fixed in place and then one solves the many-electron problem for this set of positive charge centers.

## 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

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

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

### Physics

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$a = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10} \text{ m} \qquad \mathrm{E_n} = -\left[ \frac{\mathrm{m}}{2\hbar^2} \left( \frac{\mathrm{e}^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{\mathrm{n}^2} \equiv \frac{\mathrm{E}_1}{\mathrm{n}^2} \qquad \text{for} \quad \mathrm{n} = 1, 2, 3, \ldots$$

where $E_1 = -13.6$ eV.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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