Phys 3820, Fall 2011
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

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

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

We would expect V_0 to be small compared to the ground state energy for the box, namely

$$V_0 \ll E_1 = \frac{\pi^2\hbar^2}{2ma^2}$$

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*.

For the ground state ($n = 1$) we have

$$\psi_1 = \sqrt{\frac{2}{a}}\sin(\pi x/a) \qquad E_1^0 = \frac{\pi^2\hbar^2}{2ma^2}$$

so we have

$$\begin{aligned} E^1 &= \langle\psi_1|H'|\psi_1\rangle \\ &= V_0\left(\frac{2}{a}\right)\int_0^{a/2}\sin^2(\pi x/a)\,dx = \frac{2V_0}{a}\left[\frac{x}{2} - \frac{a}{4\pi}\sin(2\pi x/a)\right]\Big|_0^{a/2} \\ &= \frac{2V_0}{a}\frac{1}{2}\frac{a}{2} = \frac{V_0}{2} \end{aligned}$$

Sort of what you'd expect.

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 with $n = 1$ for the perturbed level we have

$$\psi_1^1(x) = \sum_{m\neq 1} \frac{\langle \psi_m^0 | H' | \psi_1 \rangle}{E_1^0 - E_m^0} \psi_m^0(x)$$

Substituting stuff,

$$\begin{aligned} \psi_1^1(x) &= \frac{2ma^2}{\pi^2\hbar^2} \sum_{m\neq 1} \left(\frac{1}{1-m^2} \right) \frac{2}{a} V_0 \int_0^{a/2} \sin(m\pi x/a) \sin(\pi x/a)\, dx\, \psi_m^0(x) \\ &= -\frac{4maV_0}{\pi^2\hbar^2} \sum_{m\neq 1} \left(\frac{1}{m^2-1} \right) \int_0^{a/2} \sin(m\pi x/a) \sin(\pi x/a)\, dx\, \psi_m^0(x) \end{aligned}$$

And now we need to work out the integral in the last expression. Doing this by hand, we gets

$$\begin{aligned} \int_0^{a/2} \sin(m\pi x/a) \sin(\pi x/a)\, dx &= \left[\frac{\sin((m-1)\pi x/a)}{2(m-1)\pi/a} - \frac{\sin((m+1)\pi x/a)}{2(m+1)\pi/a} \right] \Big|_0^{a/2} \\ &= \frac{a}{2\pi} \left[\frac{-\cos(m\pi/2)}{(m-1)} - \frac{\cos(m\pi/2)}{m+1} \right] \\ &= -\frac{a}{2\pi} \cos(m\pi/2) \left[\frac{m+1-(m-1)}{m^2-1)} \right] \\ &= -\frac{a\cos(m\pi/2)}{\pi(m^2-1)} \end{aligned}$$

Use

$$\cos(m\pi/2) = \begin{cases} 0 & m \text{ odd} \\ (-1)^{m/2} & m \text{ even} \end{cases}$$

and put everything back. Get

$$\psi_1^1(x) = \frac{4ma^2V_0}{\pi^3\hbar^2} \sum_{m \text{ even}} \frac{(-1)^{m/2}}{(m^2-1)^2} \sqrt{\frac{2}{a}} \sin(m\pi x/a)$$

2. Two identical bosons are placed in a harmonic oscillator well (potential $V(x) = \frac{1}{2}m\omega^2x^2$). They interact weakly via a very weak potential of the form

$$V(x_1, x_2) = \lambda(x_2 - x_1)^2$$

where λ is some "small" constant.

a) Ignoring the interaction between the particles, find the ground state (wave function and energy) of this system.

For the noninteracting system, the ground state wave function is just the product of two single--particle wave functions for the harmonic oscillator:

$$\psi_{\mathrm{gs}}(x_1, x_2) = \psi_0(x_1)\psi_0(x_2) = \sqrt{\frac{m\omega}{\pi\hbar}} e^{-\frac{m\omega}{2\hbar}x_1^2} e^{-\frac{m\omega}{2\hbar}x_2^2}$$

The ground state energy is just the sum of energies of two indp't oscillators,

$$E^0_{\rm gs} = \tfrac{1}{2}\hbar\omega + \tfrac{1}{2}\hbar\omega = \hbar\omega$$

b) Use first–order perturbation theory to estimate the effect of the particle-particle interaction on the energy of the ground state. (Set it up; get as far as you can with the calculating.)

The first-order energy correction is

$$\begin{aligned}
E^1_{\rm gs} &= \int\int |\psi(x_1, x_2)|^2 \lambda (x_2 - x_1)^2 \, dx_1 \, dx_2 \\
&= \lambda \frac{m\omega}{\pi\hbar} \int\int (x_2 - x_1)^2 e^{-(m\omega x_1^2/\hbar)} e^{-(m\omega x_2^2/\hbar)} \, dx_1 \, dx_2 \\
&= \lambda \frac{m\omega}{\pi\hbar} \int\int (x_2^2 + x_1^2 - 2x_1 x_2) e^{-(m\omega(x_1^2+x_2^2)/\hbar)} \, dx_1 \, dx_2
\end{aligned}$$

Now we note that the cross term is odd in both x_1 and x_2 so that term in the integral will give zero. As for the terms with the x_1^2 and x_2^2 factors, we note that switching the (dummy) variables x_1 and x_2 in one gives the other term, so just evaluate it once with a factor of 2. This leaves:

$$\begin{aligned}
E^1_{\rm gs} &= 2\frac{\lambda m\omega}{\pi\hbar} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} x_2^2 e^{-(m\omega(x_1^2+x_2^2)/\hbar)} \, dx_1 \, dx_2 \\
&= \frac{2\lambda m\omega}{\pi\hbar} \left[2\sqrt{\pi} \left(\tfrac{1}{2} \sqrt{\frac{\hbar}{m\omega}} \right) 2\sqrt{\pi}\, 2 \left(\tfrac{1}{2} \sqrt{\frac{\hbar}{m\omega}} \right)^3 \right] \\
&= \frac{\lambda m\omega}{\pi\hbar} \left[\pi \left(\frac{\hbar}{m\omega} \right)^2 \right]
\end{aligned}$$

and this gives the very simple

$$E^1_{\rm gs} = \frac{\lambda\hbar}{m\omega}$$

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

$$E^1_i = \langle \psi^0_i | H' | \psi^0_i \rangle$$

when ψ^0_i is a member of a set of degenerate states.

The problem is that the particular $linear\ combination$ of the degenerate states that we might start with is $arbitrary$ and when the perturbation is applied, they may not be the states that the new $non\text{-}degenerate$ states are similar to. Thus the new wave functions do not have a "small" difference from the original states.

b) In solving for the first-order energy perturbations of a set of degenerate states you construct the W matrix. How do we find the elements of W and what do we do with this matrix in order to get the first-order energy corrections for the perturbed system?

The W matrix is just the matrix made of matrix elements of H' amonst the original degenerate states that we have in hand:

$$W_{ij} = \langle \psi_i | H' | \psi_j \rangle$$

The values of E^1 which gives the energies of the new states via $E = E^0 + E^1$ are the eigenvalues of Q.

4. 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.

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?)

We wrote an expansion for the *relativistic* kinetic energy ($T = E - mc^2$) in terms of the (relativistic!) momentum. Then we guessed that all along $\frac{\hbar}{i}\frac{\partial}{\partial x}$ was the operator for the *relativistic* momentum and substituted for $\mathbf{p}$ wherever it occurred. The handling of p^4 required a little more guesswork!

In the end, the replacement of an algebraic expression with a nasty square root by operators is guessing. The Dirac equation for the electron is now known to be the right way to do this and in addition it predicts the spin of the electron and the existence of antiparticles.

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

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

The spin-orbit effect can be understood by considering the physics in the somewhat-illegal reference frame of the orbiting electron. There it seems that the orbiting proton gives a magnetic field (proportional to $\mathbf{L}$) with which the electron's magnetic moment (proportional to $\mathbf{S}$) can interact.

b) 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

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

Use the vector relation

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

Then But for state of "good" $\mathbf{J}^2$, $\mathbf{L}^2$ and $\mathbf{S}^2$ the operators give

$$\mathbf{J}^2 = \hbar^2 j(j+1) \qquad \mathbf{L}^2 = \hbar^2 l(l+1) \qquad \mathbf{S}^2 = \hbar^2 s(s+1) = \frac{3}{4}\hbar^2$$

Then the effect of the operator $\mathbf{L}\cdot\mathbf{S}$ is

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

6. How is the strong–field Zeeman calculation different from the weak–field one?

The weak field case meant that the spin-orbit effect is a stronger perturbation of the naive H atom so that the proper states to now perturb with the external B field are those of L coupled to S to give eigenstates of J^2 and m_j.

For the strong field case we go back to perturbing states with "good" m_l and m_s which are split by the strong B field and then the spin-orbit effect is a perturbation on *those* states.

7. Very briefly, what is the Stark Effect (in atoms)?

It is a shift in the energy levels of an atom due to an external *electric* field. We didn't cover it, though Griffiths made an exercise out its application to the H atom.

The problem is marked by the peculiarity that a uniform electric field gives a potential the goes as negative you want at big distances so that an electric has a finite probablity of tunneling out of the stomic environment.

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

The "line" arises from the transition between the two narrowly--split hyperfine structure states of the 1s state of the hydrogen atom, of which there is lots in outer space. The transition is between the states where the spins of the proton and electron are aligned and where they are un-aligned. Being such a small energy difference, the corresponding photon is in the radio part of the EM spectrum.

9. 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 $0 \le x \le a$,

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

a) Find A

The wave function must be normalized, so

$$\begin{aligned}\int_0^a |\psi(x)|^2\,dx &= A^2\int_0^a x^2(a-x)^2\,dx = A^2\int_0^a (a^2x^2-2ax^3+x^4)\,dx \\ &= A^2\left[a^2\frac{x^3}{3}-2a\frac{x^4}{4}+\frac{x^5}{5}\right]\Big|_0^a = A^2a^5\left[\frac{1}{3}-\frac{1}{2}+\frac{1}{5}\right] = A^2\frac{a^5}{30} = 1\end{aligned}$$

So then

$$A = \sqrt{\frac{30}{a^5}}$$

b) What upper bound does this trial function give on the ground state energy? How far off is it?

For this problem we have

$$\langle H\rangle = \langle T\rangle = -\frac{\hbar^2}{2m}\frac{30}{a^5}\int_0^a x(a-x)\frac{d}{dx}[x(a-x)]\,dx$$

which is simple!

$$\langle H\rangle = -\frac{30\hbar^2}{2ma^5}\int_0^a x(a-x)(-2)\,dx = \frac{30\hbar^2}{ma^5}\left[a\frac{x^2}{2}-\frac{x^3}{3}\right]\Big|_0^a = \frac{30\hbar^2}{6ma^5}$$

So we have found

$$E_{\rm gs} \le \langle H\rangle = \frac{5\hbar^2}{ma^2}$$

butthe exact answer is known! It is

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

and since $5 \ge \frac{\pi^2}{2}$ the variational bound is indeed bigger than the true ground state energy, by about 1.3%.

10. Using the variational principle, prove that first–order non-degenerate perturbation theory always *overestimates* (or at any rate never *underestimates*) the ground state energy. *Explain the steps in your reasoning.*

With H taken to be a slightly perturbed version of a problem with Hamiltonian H_0 with $H' = H_0 + H'$, we consider the ground state of the unperturbed system ψ_0, where $H_0\psi_0 = E_0$. As this is not an eigenfunction of H (but is assumed to satisfy the same boundary conditions) it can serve as a trial function $\psi_{\rm tr}$ for the ground state of H. The variational principle then give

$$\begin{aligned}E_{\rm gs} &\le \langle H\rangle_{\psi_0} = \langle\psi_0|H|\psi_0\rangle = \langle\psi_0|H_0|\psi_0\rangle + \langle\psi_0|H'|\psi_0\rangle \\ &= E_0 + \langle\psi_0|H'|\psi_0\rangle\end{aligned}$$

but here the right hand side is just the value of the ground state energy *to first order in perturbation theory*, since $\langle\psi_0|H'|\psi_0\rangle = E_0^1$.

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 B-O approximations states that we can treat the nuclei of an atomic or molecular problem as being fixed in place; we can calculate an *electronic* energy for this configuration and (for a molecule) later vary the geometry of the placement of the nuclei to get a total energy for the system.

Useful Equations

Math

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

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

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

Numbers

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

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

Physics

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$Y_0^0=\sqrt{\frac{1}{4\pi}} \qquad Y_1^0=\sqrt{\frac{3}{4\pi}}\cos\theta \qquad Y_1^{\pm1}=\mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}$$

$$Y_2^0=\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1) \qquad Y_2^{\pm1}=\mp\sqrt{\frac{15}{8\pi}}\sin\theta\,\cos\theta e^{\pm i\phi} \qquad Y_2^{\pm2}=\sqrt{\frac{15}{32\pi}}\sin^2\theta\,e^{\pm2i\phi}\text{etc.}$$

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

$$a=\frac{4\pi\epsilon_0\hbar^2}{me^2}=0.529\times10^{-10}\text{ m} \qquad E_n=-\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}\equiv\frac{E_1}{n^2} \qquad \text{for}\quad n=1,2,3,\ldots$$

where $E_1=-13.6$ eV.

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

$$\lambda f=c \qquad E_\gamma=hf \qquad \frac{1}{\lambda}=R\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right) \qquad \text{where} \qquad R=\frac{m}{4\pi c\hbar^3}\left(\frac{c^2}{4\pi\epsilon_0}\right)^2=1.097\times10^7\text{ m}^{-1}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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