Final Exam, Quantum Mechanics
Due: end of finals week.

1. van der Waals force and the H_2 molecule.

a. Let H be the hamiltonian operator appropriate for two hydrogen nuclii whose locations are fixed and whose distance is R and two electrons. Use atomic units. In particular, R will be a multiple of the Bohr radius. Write an expression for H.

b. Consider the 4 dimensional space spanned by $|\uparrow\uparrow\rangle$, $|\downarrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, and $|\downarrow\downarrow\rangle$. Here, for example, $|\downarrow\uparrow\rangle$ means that the z component of the spin of electron 1 is $-\frac{1}{2}$ and the z component of the spin of electron 2 is $+\frac{1}{2}$. Show that the action of $O(3)$ on this space decomposes into an irreducible representation of dimension one spanned by $|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle$, and a three dimensional representation whose σ_z states are, $|\uparrow\uparrow\rangle$, $|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle$, $|\downarrow\downarrow\rangle$. To see this, the total spin, σ, is the sum of the spins of the indivisidual electrons. For example, $\sigma_x = \sigma_x^{(1)} + \sigma_x^{(2)}$ where, for example,

$$\sigma_x^{(1)}\,|\uparrow\downarrow\rangle = -\frac{i}{2}\,|\downarrow\downarrow\rangle \ .$$

It will be convenient again to use the operator that raises the σ_z eigenvalue: $\sigma_x + i\sigma_y$. These two representations are called the "singlet" and "triplet" state respectively because of what happens to the spectral lines in a magnetic field.

c. Show that the ground state wave function is a singlet state. That is, the state takes the form

$$\Phi = \Psi(x,y)\cdot(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle) \ ,$$

where x and y are the coordinates of the two electrons. We call Ψ the "orbital" part of the state and the second factor the spin part (duh!). The orbital part satisfies the Schrödinger PDE eigenvalue problem since our H from part a does not involve spin explicitly. Hint: show that Φ has fermionic symmetry if $\Psi(x,y) = \Psi(y,x)$. If I minimize the "orbital" Rayliegh quotient without regard to symmetry, what symmetry should the minimizing orbital wave function have? If I used a Φ with some other spin depencende, what orbital eigenfunctions would I have to use?

Remark: The spin state $|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle$ has come to be called "entangled" because learning something about the spin of electron 1 tells us about electron 2. One of the most famous philosophical difficulties in quantum mechanics is the Einstein, Pedulski, Rosen paradox. In this paradox we somehow imaging breaking the molecule, sending the electrons off in opposite directions without altering their spin state. In the past ten years, this has actually been done experimentally. When the electrons are far apart, we measure the spin (σ_z) of electron 1. If this $+\frac{1}{2}$ then we know that electron 2 will have spin $-\frac{1}{2}$. Before we measure electron 1, electron 2 could have either spin and the spins are equally likely. After measuring electron 1, the spin of electron 2 is determined. This sure seems like the measurement of electron 1 is somehow influencing electron 2, and faster than the speed of light. In recent experiments, this is exactly what happens. This question shows that tangled states are not exotic or hard to make, just put a helium atom or H_2 molecule in its ground state.

d. Let $E(R)$ be the ground state energy of the H_2 molecule with deparation R. Then $E(R) \to E_0$ as $R \to \infty$, where E_0 is the ground state energy of two "separated" hydrogen atoms, "obvoiusly" twice the hydrogen atom ground state energy. We want to estimate $E(R)$ for large R by a combination of perturbative and variational techniques. We write $\phi(x)$ for the single electron (orbital) wave function that is the ground state for the hydrogen atom, and $\phi_1(x)$ for this wave function centered at nucleus 1, etc. Show that the wave function

$$\Psi_0(x,y) = \frac{1}{2}\left(\phi_1(x)\phi_2(y) + \phi_2(x)\phi_1(y)\right)$$

has Rayleigh quotient $E_0 + O(e^{-cR})$ for some positive c. What does this wave function say about the relative locations of the two electrons? Do you think this is a natural start in finding the large R two electron ground state?

e. Show that

$$H\Psi_0 = E_0\Psi_0 + \frac{1}{R^3}f(x,y) + \frac{1}{R^4}g(x,y) + \cdots ,$$

where $\langle f \mid \Psi_0\rangle = 0$, etc. Hint: This is basically Taylor series. First work out $(R^2+t)^{-1/2} \sim \frac{1}{R} + \frac{?t?}{R^2} + \cdots$. Now think of applying H to $\phi_1(x)\phi_2(y)$. Of the five terms in the potential energy (don't forget the nuclear repulsion), one helps make E_0 and the other have "far field" expansions that vanish when x is at nucleus one and y is at nucleus 2. The first two terms in the se expansions cancel leaving $1/R^3$ terms that only partly cancel. Don't worry about the form of g. If you do the expansion carefully, it will be clear that $\langle g \mid \Psi_0\rangle = 0$, and also for the later terms.

f. Use the result of part e to show that there is a correction to Ψ_0 of the form $\frac{1}{R^3}\Psi_3(x,y)$. Hint: use the orthogonality relation.

g. Show that the Rayleigh quotient fo $\Psi_0 + \frac{1}{R}\Psi_3$ has the form $E_0 - \frac{c}{R^6}$ where $c > 0$. This is the famous van der Waals $1/R^6$ attraction between neutral atoms.

h. Make an one line abstract argument that if there is an expansion $E(R) \sim E_0 = \frac{c}{R^p}$, then $c \geq 0$.

2. Suppose we treat the proton in the hydrogen atom quantum mechanically instead of fixing its position. Then we would seek a two body wave function $\phi(x, y)$, where x is the electron position and y is the proton position. If we put a single pair in a large box of side L, we imagine the ground state takes the form $f((x+y)/2) \cdot g((x-y)/2)$. Here g would be something like the hydrogen atom ground state wave function and f would be the ground state for a single particle confined to a box. In this particular example, it is slightly better to replace, say, $(x+y)/2$ by the mass weighted average $(m_e x + m_p y)/(m_e + m_p)$. Now suppose we have n electrons and n protons in a large box.

a. Show that the wave function

$$\Psi(x_1, y_1, x_2, y_2, \ldots, x_n, y_n) = \det\left(\phi(x_j, y_k)\right)$$

has the desired Fermionic symmetry for electron or proton exchange. Here we write $\det(a_{jk})$ to be the determinant of the matrix whose elements are a_{jk}.

b. Explain how this illustrates the often repeated statement that if you look at identical atoms each made of an even number of fermions, then that atom looks like a boson.

3. Consider a hydrogen atom in a weak periodic electric field in the x_1 direction:

$$V(x, t) = \frac{-1}{|x|} + \epsilon x_1 \cos(\omega t) \ .$$

a. What is the anologue of the Bloch wave ansatz for the time dependence of solutions to the time dependent Schrödinger equation?

b. For small ϵ and ω not an eigenvalue of the unperturbed problem, find the approximate form of the solution, including the first correction term.

4. (Optional but interesting) The electron affinity of an atom is the energy added by adding one more electron to the neutral atom. This means Z protons and $Z+1$ electrons. Give a variational argument (with an explicit computation with some trial function) to show that this affinity is positive. For example, the energy a proton with two electrons is less (more negative) than the energy with a single electron.