Physics 828 Problem Set 6 Due Wednesday 02/24/2010

(6.1)(a) Here is the question asked in class. When we computed the expectation values of the kinetic and potential energies for the hydrogen atom with a Gaussian trial wave function they did not obey the Virial theorem. Why not? This is obvious if you look at the problem you solved earlier. (1 point).

In the problem you showed the Virial theorem assuming that the states used are stationary states or eigenstates of the Hamiltonian. In our calculation we used Gaussian trial wave functions that are not stationary states.

(b) For the hyperfine interaction you considered in problem set 4 the singlet lies lower than the triplet. Explain why this is so from elementary physics. (2 points)

This problem will not be graded. Shankar's problem gives a good estimate but the origin of the interaction is more subtle. This problem will be re-assigned after we discuss the hyperfine interaction in class.

(c) What is the ionization energy of Helium? You may assume that the ground state energy of the helium atom is $-78.975\,eV$. Note that the ground state energy is not what is directly measured. Convert the value in eV into chemists' units of $kJ/mole$. If your answers are off by more than 5% you get zero credit. (3 points)

What is measured is not the ground state energy but the **ionization energy**. This is the energy required to remove the most weakly bound electron from the atom. It is given by the difference $E_{ion} - E_{atom}$.
First the energy of the helium ion. A singly ionized Helium atom looks like a hydrogen atom with a nuclear charge 2. The latter has an energy $-4 \times 13.6eV$ as you did on the midterm.

Given that the ground state energy is $-78.975\,eV$ we obtain for the ionization energy $-54.4 + 78.975 \approx 24.6\,eV \approx 2374\,kJ/mol$.

We have $1eV = 1.60217653(14) \times 10^{-19}J$ and the Avogadro number is $6.0221415(10) \times 10^{23}$. Thus

$$1\,\frac{eV}{atom} = 1.60217653(14) \times 10^{-19} \cdot 6.0221415(10) \times 10^{23} = 96.4853\,\frac{kJ}{mol}\,.$$

I tend to remember $1\,kJ/mole \approx 0.01eV/atom$ which is within 5%. .

(d) One of the (unnormalized) trial wave functions that was tried for the ground state of Helium with a spin singlet was

$$e^{-Z_1 r_1 - Z_2 r_2} + e^{-Z_1 r_2 - Z_2 r_1}$$

a symmetric spatial wave function with two variational parameters Z_1 and Z_2. The variational minimum occurs for $\{Z_1, Z_2\} = \{2.183, 1.189\}$. Why is this result surprising? This gives a better estimate than the trial wave function with $Z_1 = Z_2$. Explain why this trial wave function does better. (2 points)

What surprised me was that a system that is completely symmetric in the two electrons has a variational minimum that appears to break the symmetry. Of course, this is only apparent since the wave function is indeed symmetric.

One of the electrons is closer to the nucleus while the other is farther away. I did a quick calculation and found that the attractive potential energy of the nucleus is lower when $z_1 = z_2$. The kinetic energy of the inner electron is higher because it is more localized while that of the outer electron is decreases. However, the electrons are farther apart in this configuration reducing Coulomb repulsion considerably more than the loss in the other terms. Thus this correlation gives a better energy.

One cannot over-interpret the meaning of the variational parameters. Why?

I plotted my solution (yeah, I did the integrals) and it is displayed on the next page.

(e) Construct a trial wave function to determine the energy of the excited state of Helium in which one of the electrons has been promoted to the 2p state. Explain the logic behind your choice clearly. Use two variational parameters. The actual calculation is long and used to be assigned in courses long, long ago. (3 points)

The two possibilities are singlet and a triplet spin states with the corresponding spatial wave functions

$$\Psi_\pm = N_\pm \left(\phi_{1s}(\vec{r}_1)\,\phi_{2p}(\vec{r}_2) \pm \phi_{1s}(\vec{r}_2)\,\phi_{2p}(\vec{r}_1)\right)$$

with appropriate overall symmetry. We can use trial functions

$$\phi_{1s}(\vec{r}) = e^{-\alpha r}$$

$$\text{and} \quad \phi_{2p}(\vec{r}) = r\, e^{-\beta r} \cos\theta$$

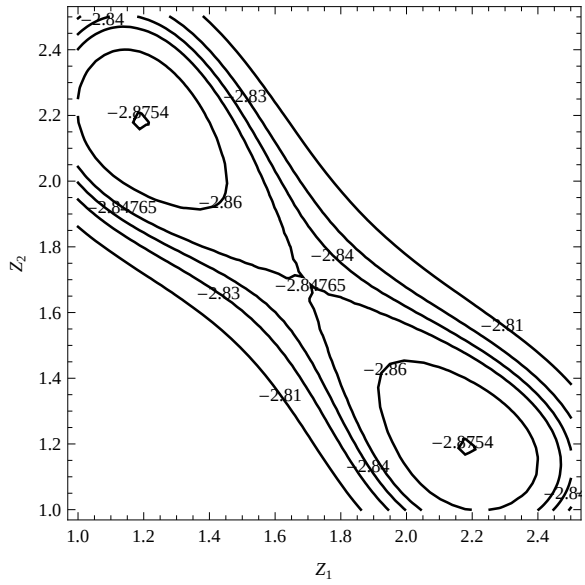


Figure 1: The contour plot of values of $\{Z_1, Z_2\}$ and the associated energy values. There is a saddle point at $Z_1 = Z_2 = 1.69$ and the minimum occurs at $Z_1 = 2.183$ and $Z_2 = 1.189$ and vice versa.

where α and β are variational parameters. The parameters are related to the effective nuclear charges seen by the electrons in the one-particle states. The normalization constants are given by

$$N_{\pm}^2 \;=\; \frac{2\pi^2}{\alpha^3\beta^5}\,.$$

As in the arguments presented in class $\Psi_-(\vec{r}_1, \vec{r}_2)$ vanishes when $\vec{r}_1 = \vec{r}_2$ and is small in its vicinity. This reduces the electrostatic repulsion between the electrons. Thus one would expect the triplet to correspond to the lowest energy excited states in this manifold. All this is not obviously true since Hund's rules apply to the ground state and not the excited states. The experiment confirms that the triplet is lower than the singlet by $0.254\,eV$ according to NIST data. In our approximation the triplet itself is degenerate. The degeneracy is lifted by the spin-orbit interaction.

(f) Cr^{3+} **ion:** *These ions give ruby its red color when they substitute for Al in an* Al_2O_3 *matrix. The energy level structure in the crystal is different from that of the free ion and we will investigate this later. For this problem assume that the electronic configuration is* $3d^3$ *and apply Hund's rules to determine the ground state term structure of the free ion.. (4 points)*

We have three spins in the same sub-shell and Hund's first rule yields maximal value of the total spin $S = 3/2$.

By the second rule, the L value is the maximum possible subject to the Pauli exclusion principle. Consider $m_{s_1} = m_{s_2} = m_{s_3} = 1$. Since for the one-particle state $\ell = 2$ we can choose $m_{\ell_1} = 2$, $m_{\ell_2} = 1$ (we are trying to maximize M_L but we cannot make $m_{\ell_2} = 2$ because it would violate the Pauli Prinzip and we choose the next highest possible value) and $m_{\ell_3} = 0$. This yields $M_L = 3$ yielding $L = 3$. So far the term structure is ${}^4F$ where the left superscript is $2S + 1$; the letter corresponds to $L = 3$.

We use Hund's third rule yields minimum value of J for less than half-fillesd shell. Thus $J = |L - S| = 3/2$. This yields $\boxed{{}^4F_{3/2}}$.

Note that the first two rules determine S and L leaving the state $(2L+1)(2S+1)$ degenerate. These can be classified according to the total angular momentum value J which can assume values ranging from $|L - S|$ up to $L + S$. This degeneracy is lifted by the spin-orbit interaction $\lambda_{fs}\, \vec{L} \cdot \vec{S}$. For less than half-filled shells $\lambda_{fs} > 0$ and this makes makes the total angular momentum J assume the least possible value. What is the degeneracy now? How might one lift this degeneracy?

(g) We discussed the exchange term for two electrons in the singlet and triplet spin states in class. Consider the following wave function

$$\begin{vmatrix} \phi_a(\vec{r}_1)\alpha_1 & \phi_b(\vec{r}_1)\beta_1 \\ \phi_a(\vec{r}_2)\alpha_2 & \phi_b(\vec{r}_2)\beta_2 \end{vmatrix}$$

where $\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ *represents the up-spin state and* β *represents the down spin state. Write down the expectation value of the Coulomb repulsion term in the Hamiltonian* $\frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|}$ *for this state. What is the exchange term in this case? State your result in words. (3 points)*

We will write the expectation value of the Coulomb term in the more explicit form[1]

[1] Just to belabor this we write

$$\psi(\vec{r}_1, s_1) = \phi_a(\vec{r}_1)\, \chi_a(s_1)$$

where χ_a is a two-component spinor with $s_1 = 1$ being the up-component and $s_1 = -1$ the down-spin component. Here $\vec{r}_1$ denotes the position and $s_1 = \pm 1$. So $|psi(\vec{r}_1 = \vec{r}_A,\, s_1 = 1)|^2 = |\phi_a(\vec{r}_A)|^2\, |\chi_a(1)|^2$ is the probability density for finding the electron at $\vec{r}_A$ with spin up.

$$\sum_{s_1}\sum_{s_2}\int d^3r_1\int d^3r_2\,\left(\phi_a^*(\vec{r}_1)\phi_b^*(\vec{r}_2)\alpha^\dagger(s_1)\beta^\dagger(s_2)\,-\,\phi_a^*(\vec{r}_2)\phi_b^*(\vec{r}_1)\alpha^\dagger(s_2)\beta^\dagger(s_1)\right)\times$$

$$\frac{q^2}{4\pi\epsilon_0}\times(\phi_a(\vec{r}_1)\phi_b(\vec{r}_2)\alpha(s_1)\beta(s_2)\,-\,\phi_a(\vec{r}_2)\phi_b(\vec{r}_1)\alpha(s_2)\beta(s_1))\,.$$

Note that we integrate over the spatial coordinates and sum over the spin variables. You should be clear about this.
The cross terms which yield the exchange term contain

$$\sum_{s_1}\alpha^\dagger(s_1)\,\beta(s_1)\,=\,(1,\,0)\cdot\begin{pmatrix}0\\1\end{pmatrix}\,=\,0\,.$$

Thus the exchange term vanishes if the spins of the two states of the pair of electrons is different: one is up (α) and the other is down (β)..

I was reading the classic book "*Intermediate Quantum Mechanics*" by Hans Bethe and Roman Jackiw while preparing the lectures: when they derive the Hartree-Fock equations for an N-electron system they observe "that the exchange term is 0 unless the spins are the same for the two states of each pair." I wanted you to demonstrate this in the two particle case. They use the notation $\int d\tau_1$ for label 1 and say "The integration is over space and spin coordinates."

2. Find the ground state of three spin-1/2 particles at the vertices of a triangle with antiferromagnetic interactions.

$$H\,=\,\frac{4A}{3\hbar^2}\,(\vec{S}_1\cdot\vec{S}_2\,+\,\vec{S}_2\cdot\vec{S}_3\,+\,\vec{S}_3\cdot\vec{S}_1)\,.$$

Find the energy eigenvalues and their degeneracies given that $A>0$.
Compute the partition function at temperature T. Please look up any undergraduate statistical mechanics textbook. If you are interested in quantum magnetism you can think about larger S values and what happens in the classical spin system. (5 points)

We write the Hamiltonian in terms of the total spin denoted by $\vec{S}_t$:

$$\begin{aligned}H\;&=\;\frac{4A}{3\hbar^2}\,(\vec{S}_1\cdot\vec{S}_2\,+\,\vec{S}_2\cdot\vec{S}_3\,+\,\vec{S}_3\cdot\vec{S}_1)\\&=\;\frac{2A}{3\hbar^2}\,\left(\vec{S}_t\cdot\vec{S}_t\,-\,\vec{S}_1\cdot\vec{S}_1\,-\,\vec{S}_2\cdot\vec{S}_2\,-\,\vec{S}_3\cdot\vec{S}_3\right)\\&=\;\frac{2A}{3\hbar^2}\,\left(\vec{S}_t\cdot\vec{S}_t\,-\,3\hbar^2\frac{3}{4}\right)\end{aligned}\qquad(1)$$

since we know that for a spin-1/2 particle $\vec{S} \cdot \vec{S} = \hbar^2 \frac{1}{2} \left(\frac{1}{2} + 1 \right)$.

The sum of the three spins yields $S_t = 3/2$ or $S_t = 1/2$ with two such doublets. Since $\frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0$ when we add 1/2 to the result we get 3/2 and 1/2 from $S = 1$ and another 1/2 from $S = 0$.
Thus for the $S = 3/2$ states $\vec{S}_t \cdot \vec{S}_t = \hbar^2 \frac{3}{2} \frac{5}{2}$ and so the energy is A.
For the $S = 1/2$ states $\vec{S}_t \cdot \vec{S}_t = \hbar^2 \frac{1}{2} \frac{3}{2}$ and so the energy is $-A$. These form the ground-state energy.

The two doublets have interesting eigenvectors. It is a good theoretical exercise to find the ground state wave functions and characterize them. This is the baby version of what is called a frustrated quantum magnet. Condensed matter theorists have studied a triangular lattice of such spin-1/2 objects.

Since we have 4 states each with energy $+A$ and 4 with energy $-A$ the partition function is

$$Z \; = \; 4\, e^{\beta A} \; + \; 4 e^{-\beta A} \; = \; 8 \, \cosh(\beta A)$$

where $\beta \equiv 1 \frac{1}{k_B T}$. There is a gap in the energy spectrum and the model yields a Schottky-like specific heat.

3. Since there was some question about whether we had studied resonance please do Shankar 14.4.3 on page 396. Explain the resonance phenomenon clearly. (6 points)

Here is brief sketch of the solution:
From the Schrödinger equation in the stationary or laboratory frame,

$$i\hbar \frac{d}{dt} |\psi(t)\rangle \; = \; H \, |\psi(t)\rangle \, ,$$

using the definition of the state vector in the rotating frame,

$$|\psi_r(t)\rangle \; = \; e^{-i\omega t S_z/\hbar} \, |\psi(t)\rangle \, ,$$

we obtain the evolution equation in the rotating frame:

$$i\hbar \frac{d}{dt} |\psi_r(t)\rangle \; = \; \left(\omega S_z \; + \; e^{-i\omega t S_z/\hbar} H e^{i\omega t S_z/\hbar} \right) \, |\psi_r(t)\rangle$$

Given that

$$H \; = \; -\gamma \vec{S} \cdot \vec{B} \; = \; -\gamma \left(B_0 \cos(\omega t) \, S_x \; - \; B_0 \sin(\omega t) \, S_y \; + \; B_0 S_z \right)$$

we evaluate $e^{-i\omega t S_z/\hbar} H e^{i\omega t S_z/\hbar}$. First we write

$$H \;=\; -\frac{\gamma B\hbar}{2}\begin{pmatrix} 0 & e^{i\omega t} \\ e^{-i\omega t} & 0 \end{pmatrix} \;-\; \gamma B\, S_z\,.$$

Note that the S_z term in H is unaffected by the transformation. Using

$$e^{i\alpha\sigma_z} \;=\; \cos\alpha\, I \;+\; i\sin\alpha\,\sigma_z \;=\; \begin{pmatrix} e^{i\alpha} & 0 \\ 0 & e^{-i\alpha} \end{pmatrix}$$

we have

$$e^{-i\omega t S_z/\hbar} H e^{i\omega t S_z/\hbar} \;=\; -\frac{\gamma B\hbar}{2}\begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix}\begin{pmatrix} 0 & e^{i\omega t} \\ e^{-i\omega t} & 0 \end{pmatrix}\begin{pmatrix} e^{i\omega t/2} & 0 \\ 0 & e^{-i\omega t/2} \end{pmatrix} - \gamma B\, S_z\,.$$

Trivial multiplication yields an expected time-independent expression

$$e^{-i\omega t S_z/\hbar} H e^{i\omega t S_z/\hbar} \;=\; -\gamma B\, S_x \;-\; \gamma B_0\, S_z\,.$$

Substituting this back into the Schrödinger equation in the rotating frame we obtain

$$i\hbar\frac{d}{dt}|\psi_r(t)\rangle \;=\; \left[-\gamma B S_x \;-\; \gamma\left(B_0 \;-\; \frac{\omega}{\gamma}\right) S_z\right]|\psi_r(t)\rangle \;=\; -\gamma\vec{B}_r\cdot\vec{S}\,|\psi_r(t)\rangle$$

where the effective field in the rotating frame agrees with the classical expression given in Shankar 14.4.29.

Since we have a time-independent Hamiltonian in the rotating frame the time evolution operator can be obtained easily using the identity

$$e^{i\alpha\hat{n}\cdot\vec{\sigma}} \;=\; \cos\alpha\, I \;+\; i\hat{n}\cdot\vec{\sigma}\,.$$

The unitary evolution operator or propagator is given by

$$U_r(t) \;=\; e^{i\frac{\gamma B_r}{2}\,\hat{n}\cdot\vec{\sigma}} \quad \text{where} \quad \hat{n} \;=\; \frac{\vec{B}_r}{B_r}$$

and $B_r \;=\; |\vec{B}_r|$. Defining $\omega_r \equiv \gamma B_r$ and $\omega_0 \equiv \gamma B_0$ the propagator can be written explicitly as[2]

$$U_r(t) \;=\; \cos(\omega_r t/2)\, I \;+\; i\sin(\omega_r t/2)\,\left(\frac{\gamma B}{\omega_r}\,\sigma_x \;+\; \frac{\omega_0-\omega}{\omega_r}\,\sigma_z\right)$$

[2]

$$\hat{n} \;=\; \frac{\vec{B}_r}{B_r} \;=\; \frac{B}{B_r}\hat{x} \;+\; \frac{B_0-(\omega/\gamma)}{B_r}\hat{z} \;=\; \frac{\gamma B_r}{\omega_r}\hat{x} \;+\; \frac{\omega_0-\omega}{\omega_r}\hat{z}\,.$$

Given $|\psi(t=0)\rangle = |\psi_r(t=0)\rangle = |z+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ we have

$$|\psi_r(t)\rangle = U_r(t)|\psi_r(t=0)\rangle = \begin{pmatrix} \cos(\omega_r t/2) + i\frac{\omega_0-\omega}{\omega_r}\sin(\omega_r t/2) \\ i\frac{\gamma B}{\omega_r}\sin(\omega_r t/2) \end{pmatrix}$$

by trivial matrix multiplication.

We can rotate back to the lab frame using

$$|\psi(t)\rangle = e^{i(\omega t/2)\sigma_z} = \begin{pmatrix} e^{i\omega t/2} & 0 \\ 0 & e^{-i\omega t/2} \end{pmatrix}.$$

Thus yields 14.4.36.

On resonance $\omega = \omega_0$ and $B_r = B$. We write $\gamma B = \omega_1$ as is usually done. Then equation 14.4.36 becomes

$$|\psi(t)\rangle = \begin{pmatrix} \cos(\omega_1 t/2)\, e^{i\omega_0 t/2} \\ i\sin(\omega_1 t/2)\, e^{-i\omega_0 t/2} \end{pmatrix}.$$

The state $|\hat{n}\rangle$ is given by

$$|\hat{n}\rangle = \begin{pmatrix} \cos(\theta/2)\, e^{-i\phi/2} \\ \sin(\theta/2)\, e^{i\phi/2} \end{pmatrix}.$$

Comparison yields $\phi = -\omega_0 t$ showing that the spin precesses at a rate $-\omega_0$ as expected. In addition $\theta = \omega_1 t$ which means that it is flipping at a slow rate ($\omega_1 << \omega_0$.) The factor of i can be understood most easily in the rotating frame. On resonance the field acts only along the x-axis and a spin initially along the z- axis precesses in the $y-z$ plane; we have

$$|\psi_r(t)\rangle = \begin{pmatrix} \cos(\omega_1 t/2) \\ i\,\sin(\omega_r t/2) \end{pmatrix}$$

or equivalently $\phi = \pi/2$.

We are asked to determine $\langle\mu_z(t)\rangle$ which is given by $\langle\mu_z(t)\rangle = \langle\psi(t)|\gamma S_z|\psi(t)\rangle$ where $|\psi(t)\rangle$ is known. A trite calculation (matrix multiplication) yields the result that agrees with the classical expression in equation 14.4.31.

4. **Extra credit:** Consider two particles in one dimension described by coordinates x_1 and x_2 with single-particle harmonic oscillator Hamiltonians:

$$H_j = \frac{P_j^2}{2m} + \frac{1}{2}m\omega_j^2 X_j^2$$

for $j = 1, 2$. Now include an interaction of the form $\lambda X_1^2 X_2^2$. Set up the Hartree equations (the coupled equations) for the ground state. Start with the guess as a product wave function of harmonic oscillator ground states. Find the "self-consistent" equations which in this case are algebraic. Solve them numerically for $\omega_1 = \omega_2 = 1$ for a couple of values of λ. (6 points)

The Hartree wave function is just a product wave function:

$$\psi(x_1,\, x_2) \;=\; \phi_a(x_1)\phi_b(x_2)\,.$$

We write the Hamiltonian as $H \;=\; H_1 + H_2 + V_{int}$ where H_1 depends only on x_1, H_2 only on x_2 and V_{int} on both coordinates. The effective Hartree potential felt by the "first" electron is $\lambda\langle X_2^2\rangle \times X_1^2$, i.e., in coordinate space

$$\langle V_{int}\rangle_{x_2} \;=\; \int_{-\infty}^{\infty} dx_2\, \phi_b^*(x_2)\, x_2^2\, \phi_b(x_2) \times x_1^2$$

and similarly the potential felt by the second electron is

$$\langle V_{int}\rangle_{x_1} \;=\; \int_{-\infty}^{\infty} dx_1\, \phi_a^*(x_1)\, x_1^2\, \phi_a(x_1) \times x_2^2$$

Thus the Hartree equations are

$$[H_1 \;+\; \lambda\langle x^2\rangle_b\, x_1^2\,]\phi_a(x_1) \;=\; \epsilon_1\phi_a(x_1)\,. \tag{2}$$

$$[H_2 \;+\; \lambda\langle x^2\rangle_a\, x_2^2\,]\phi_b(x_2) \;=\; \epsilon_2\phi_b(x_2)\,. \tag{3}$$

Thus we find that each particle still moves in a harmonic potential with a *renormalized* frequency. The renormalized oscillator potential is the bare potential augmented by the effect of the other oscillator. We can obtain the effective potential easily if we confine our attention to the ground state and use the Virial theorem

$$\frac{1}{2}m\omega_1^2\langle x_1^2\rangle \;=\; \frac{1}{4}\hbar\omega_1 \quad\Rightarrow\quad \langle x_1^2\rangle \;=\; \frac{\hbar}{m\omega_1}$$

with a similar expression for the second variable. We obtain (we use the equality of the masses $m_1 = m_2 = m$)

$$\left[H_1 \;+\; \frac{m}{2}\left(\frac{\hbar\lambda}{m^2\omega_2}\right) x_1^2\right] \phi_a(x_1) \;=\; \epsilon_1\phi_a(x_1)\,.$$

$$\left[H_2 \;+\; \frac{m}{2}\left(\frac{\hbar\lambda}{m^2\omega_1}\right) x_2^2\right] \phi_b(x_2) \;=\; \epsilon_2\phi_b(x_2)\,.$$

We should be careful in obtaining the self-consistent equations. The two oscillators start out with **bare** frequencies that we take to be equal: $\omega_1 \;=\; \omega_2 \;=\; \omega$. They are increased by an extra term that is inversely proportional to the renormalized frequency of the other oscillator.

Denoting the renormalized frequencies by Ω_1 and Ω_2 we see that the effective frequency for the two particles are given by

$$\Omega_1 \;=\; \sqrt{\omega^2 \;+\; \frac{\hbar\lambda}{m^2\Omega_2}}\,.$$

$$\Omega_2 \;=\; \sqrt{\omega^2 \;+\; \frac{\hbar\lambda}{m^2\Omega_1}}\,.$$

Make sure you understand this. It is easiest if you look at Equations (2) and (3) and see that the bare frequencies are increased by a term inversely proportional to the effective frequency of the other oscillator. We rewrite these in terms of dimensionless variables:

$$\frac{\Omega_1}{\omega} \;=\; \sqrt{1 \;+\; \frac{\frac{\hbar\lambda}{m^2\omega^3}}{\Omega_2/\omega}}\,.$$

We note that $\Lambda \equiv \frac{\hbar\lambda}{m^2\omega^3}$ is dimensionless. We have

$$\tilde{\Omega}_1 \;=\; \sqrt{1 \;+\; \frac{\Lambda}{\tilde{\Omega}_2}}$$

$$\tilde{\Omega}_2 \;=\; \sqrt{1 \;+\; \frac{\Lambda}{\tilde{\Omega}_1}}$$

we can iterate the two equations for different values of Λ.

For $\Lambda = 1$ the renormalized frequencies are 1.32472 times the bare frequency.
For $\Lambda = 0.5$ the renormalized frequencies are 1.19149 times the bare frequency.
If you are full of unexpended energy you can find the exact ground state energy by solving the Schrödinger equation numerically.

It is actually quite interesting to evaluate the Hartree energy. Note that it is not $\epsilon_1 + \epsilon_2$ as you might have naively guessed. Multiplying Equation (2) by $\phi_a(x_1)$ and integrating over x_1 we have

$$\langle H_1\rangle_a \;+\; \langle V_{int}\rangle \;=\; \epsilon_1$$

Similarly, the second Hartree equation yields

$$\langle H_2\rangle_b \;+\; \langle V_{int}\rangle \;=\; \epsilon_2$$

The total energy is

$$\langle H_1\rangle_a \;+\; \langle H_2\rangle_b \;+\; \langle V_{int}\rangle \;=\; \epsilon_1 \;+\; \epsilon_2 \;-\; \langle V_{int}\rangle\,.$$

For the Hartree-Fock equations the so-called Koopmans' theorem addresses the interpretation of the single-particle energies. Soon after proving this theorem (under the direction of Kramers when he was 23) Tjalling C. Koopmans became an economist and won the Nobel Memorial Prize in Economics.