CHAPTER 14

1. The spin-part of the wave function is the triplet

$$m_s = 1 \qquad \chi_+^{(1)}\chi_+^{(2)}$$

$$m_s = 0 \qquad \frac{1}{\sqrt{2}}(\chi_+^{(1)}\chi_-^{(2)} + \chi_-^{(1)}\chi_+^{(2)})$$

$$m_s = -1 \qquad \chi_-^{(1)}\chi_-^{(2)}$$

This implies that the spatial part of the wave function must be antisymetric under the interchange of the coordinates of the two particles. For the lowest energy state, one of the electrons will be in an $n = 1$, $l = 0$ state. The other will be in an $n = 2$, $l = 1$, or $l = 0$ state. The possible states are

$$\frac{1}{\sqrt{2}}\left(u_{100}(\mathbf{r}_1)u_{21m}(\mathbf{r}_2) - u_{100}(\mathbf{r}_2)u_{21m}(\mathbf{r}_1)\right) \qquad m = 1,0,-1$$

$$\frac{1}{\sqrt{2}}\left(u_{100}(\mathbf{r}_1)u_{200}(\mathbf{r}_2) - u_{100}(\mathbf{r}_2)u_{200}(\mathbf{r}_1)\right)$$

Thus the total number of states with energy $E_2 + E_1$ is 3 x 4 = 12

2. For the triplet state, the first order perturbation energy shifts are given by

$$\Delta E_{21m} = \int\int d^3r_1 d^3r_2 \,|\frac{1}{\sqrt{2}}\left(u_{100}(\mathbf{r}_1)u_{21m}(\mathbf{r}_2) - u_{100}(\mathbf{r}_2)u_{21m}(\mathbf{r}_1)\right)|^2 \frac{e^2}{4\pi\varepsilon_0\,|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$\Delta E_{200} = \int\int d^3r_1 d^3r_2 \,|\frac{1}{\sqrt{2}}\left(u_{100}(\mathbf{r}_1)u_{200}(\mathbf{r}_2) - u_{100}(\mathbf{r}_2)u_{200}(\mathbf{r}_1)\right)|^2 \frac{e^2}{4\pi\varepsilon_0\,|\mathbf{r}_1 - \mathbf{r}_2|}$$

The $l = 1$ energy shift uses tw-electron wave functions that have an orbital angular momentum 1. There is no preferred direction in the problem, so that there cannot be any dependence on the eigenvalue of L_z. Thus all three m values have the same energy. The $l = 0$ energy shift uses different wave functions, and thus the degeneracy will be split. Instead of a 12-fold degeneracy we will have a splitting into 9 + 3 states.

The simplification of the energy shift integrals reduces to the simplification of the integrals in the second part of Eq. (14-29). The working out of this is messy, and we only work out the $l = 1$ part.

The integrals $\int\int d^3r_1 d^3r_2 \to \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \int d\Omega_1 \int d\Omega_2$ and the angular parts only come through the u_{210} wave function and through the $1/r_{12}$ term. We use Eqs. (14-26) – (14-29) to get, for the direct integral

$$\frac{e^2}{4\pi\varepsilon_0}\int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 R_{10}(r_1)^2 R_{21}(r_2)^2$$

$$\int d\Omega_1 \int d\Omega_2 \left(\frac{1}{\sqrt{4\pi}}\right)^2 \left(\sqrt{\frac{3}{4\pi}}\cos\theta_2\right)^2 \sum_L P_L(\cos\theta_{12})\frac{r_<^L}{r_>^{L+1}}$$

where θ_{12} is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$. We make use of an addition theorem which reads

$$P_L(\cos\theta_{12}) = P_L(\cos\theta_1)P_L(\cos\theta_2) + 2\sum_{m=1}\frac{(L-m)!}{(L+m)!}P_L^m(\cos\theta_1)P_L^m(\cos\theta_2)\cos m\phi_2 \frac{r_<^L}{r_>^{L+1}}$$

Since the sum is over $m = 1,2,3,\ldots$ the integration over ϕ_2 eliminates the sum, and for all practical purposes we have

$$\sum_L P_L(\cos\theta_{12})\frac{r_<^L}{r_>^{L+1}} = \sum_L P_L(\cos\theta_1)P_L(\cos\theta_2)\frac{r_<^L}{r_>^{L+1}}$$

The integration over $d\Omega_1$ yields $4\pi\delta_{L0}$ and in our integral we are left with $\int d\Omega_2(\cos\theta_2)^2 = 4\pi/3$. The net effect is to replace the sum by $1/r_>$ to be inserted into the radial integral.

(b) For the exchange integral has the following changes have to be made: In the radial integral,

$$R_{10}(r_1)^2 R_{21}(r_2)^2 \rightarrow R_{10}(r_1)R_{21}(r_1)R_{10}(r_2)R_{21}(r_2)$$

In the angular integral

$$\frac{1}{4\pi}\frac{3}{4\pi}(\cos\theta_2)^2 \rightarrow \frac{3}{(4\pi)^2}\cos\theta_1\cos\theta_2$$

In the azimuthal integration again the $m \neq 0$ terms disappear, and in the rest there is a product of two integrals of the form

$$\int d\Omega \sqrt{\frac{3}{4\pi}}\cos\theta P_L(\cos\theta) = \sqrt{\frac{4\pi}{3}}\delta_{L1}$$

The net effect is that the sum is replaced by $\frac{1}{3}\frac{r_<}{r_>^2}$ inserted into the radial integral.

For the $l = 0$ case the same procedure will work, leading to

$$\frac{e^2}{4\pi\varepsilon_0}\int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \frac{1}{r_>}\left[R_{10}(r_1)R_{20}(r_2)\right]\left[R_{10}(r_1)R_{20}(r_2) - R_{10}(r_2)R_{20}(r_1)\right]$$

The radial integrals are actually quite simple, but there are many terms and the calculation is tedious, without teaching us anything about physics.

To estimate which of the($l = 0, l = 0$) or the ($l = 0$, $l = 1$) antisymmetric combinations has a lower energy we approach the problem physically. In the two-electron wave function, one of the electrons is in the $n = 1$, $l = 0$ state. The other electron is in an $n = 2$ state. Because of this, the wave function is pushed out somewhat. There is nevertheless some probability that the electron can get close to the nucleus. This probability is larger for the $l = 0$ state than for the $l = 1$ state. We thus expect that the state in which both electrons have zero orbital angular momentum is the lower-lying state.

3. In the ground state of ortho-helium, both electroNs have zero orbital angular momentum. Thus the only contributions to the magnetic moment come from the electron spin. An electron interacts with the magnetic field according to

$$H = -\frac{ge}{2m_e}\mathbf{s}_1 \bullet \mathbf{B} - \frac{ge}{2m_e}\mathbf{s}_2 \bullet \mathbf{B} = -\frac{ge}{2m_e}\mathbf{S} \bullet \mathbf{B}$$

The value of g is 2, and thus coefficient of B takes on the values $-\frac{e\hbar}{2m_e}m_1$, where $m_1 = 1,0,-1$.

4. We assume that ψ is properly normalized, and is of the form

$$|\psi\rangle = |\psi_0\rangle + \varepsilon|\chi\rangle$$

The normalization condition implies that

$$\langle\psi|\psi\rangle = 1 = \langle\psi_0|\psi_0\rangle + \varepsilon^*\langle\chi|\psi_0\rangle + \varepsilon\langle\psi_0|\chi\rangle + \varepsilon\varepsilon^*\langle\chi|\chi\rangle$$

so that

$$\varepsilon^*\langle\chi|\psi_0\rangle + \varepsilon\langle\psi_0|\chi\rangle + \varepsilon\varepsilon^*\langle\chi|\chi\rangle = 0$$

Now

$$\begin{aligned}\langle\psi|H|\psi\rangle &= \langle\psi_0 + \varepsilon\chi|H|\psi_0 + \varepsilon\chi\rangle \\ &= E_0 + \varepsilon^* E_0\langle\chi|\psi_0\rangle + \varepsilon E_0\langle\psi_0|\chi\rangle + |\varepsilon|^2\langle\chi|H|\chi\rangle \\ &= E_0 + |\varepsilon|^2\langle\chi|H - E_0|\chi\rangle\end{aligned}$$

where use has been made of the normalization condition.Thus the expectation value of H differs from the exact value by terms of order $|\varepsilon|^2$.

5. We need to calculate

$$E(\alpha)=\frac{\int_0^\infty 4\pi r^2 dr e^{-\alpha r}\left[-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right)+\frac{1}{2}m\omega^2 r^2\right]e^{-\alpha r}}{\int_0^\infty 4\pi r^2 dr e^{-2\alpha r}}$$

With a little algebra, and using $\int_0^\infty dy y^n e^{-y}=n!$, we end up with

$$E(\alpha)=\frac{\hbar^2\alpha^2}{2m}+\frac{3m\omega^2}{2\alpha^2}$$

This takes its minimum value when $dE(\alpha)/d\alpha=0$. This is easily worked out, and leads to $\alpha^2=\sqrt{3}m\omega/\hbar$. When this is substituted into $E(\alpha)$ we get

$$E_{min}=\sqrt{3}\hbar\omega$$

The true ground state energy is bound to lie below this value. The true value is $\frac{3}{2}\hbar\omega$ so that our result is pretty good.

4. The Schrodinger equation for a bound state in an attractive potential, with $l = 0$ reads

$$-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right)\psi(r)-|V_0|f(\frac{r}{r_0})\psi(r)=-E_B\psi(r)$$

With the notation $x = r/r_0$, $u_0(x) = x\,\psi(x)$, $\lambda = 2m|V_0|r_0^2/\hbar^2$; $\alpha^2=2mE_B r_0^2/\hbar^2$ this becomes

$$\frac{d^2u_0(x)}{dx^2}-\alpha^2u_0(x)+\lambda f(x)u_0(x)=0$$

Consider, now an arbitrary function $w(x)$ which satisfies $w(0)= 0$ (like $u_0(0)$) , and define

$$\eta[w]=\frac{\int_0^\infty dx\left(\left(\frac{dw(x)}{dx}\right)^2+\alpha^2w^2(x)\right)}{\int_0^\infty dx f(x)w^2(x)}$$

We are asked to prove that if $\eta = \lambda + \delta\lambda$ and $w(x) = u_0(x) + \delta u(x)$, then as $\delta u(x)$ → 0, $\delta\lambda$ → 0. We work to first order in $\delta u(x)$ only. Then the right hand side of the above equation, written in abbreviated form becomes

$$\frac{\int\left(u_0'^2+\alpha^2u_0^2\right)+2\int\left(u_0'\delta u'+\alpha^2u_0\delta u\right)}{\int f\left(u_0^2+2u_0\delta u\right)}=$$

$$=\frac{\int\left(u_0'^2+\alpha^2u_0^2\right)}{\int fu_0^2}-2\frac{\int\left(u_0'\delta u'+\alpha^2u_0\delta u\right)}{\int fu_0^2}\frac{\int\left(u_0'^2+\alpha^2u_0^2\right)}{\int fu_0^2}$$

In the above, the first term is just $\eta[u_0]$, and it is easy to show that this is just λ. The same form appears in the second term. For the first factor in the second term we use

$$\int dx\left(u_0'\delta u'\right)=\int dx\frac{d}{dx}\left(u_0'\delta u\right)-\int dx u_0''\delta u$$

The first term on the right vanishes because the eigenfunction vanishes at infinity and because $\delta u(0) = 0$. Thus the second term in the equation for $\eta[w]$ becomes

$$\frac{2}{\int fu_0^2}\int\delta u\left[-u_0''+\alpha^2u_0-\lambda fu_0\right]$$

Thus $\eta \to \lambda$ as δu → 0.

5. We want to minimize $\langle\psi|H|\psi\rangle=\sum_{i,j}a_i^*H_{ij}a_j$ subject to the condition that $\langle\psi|\psi\rangle=\sum_i a_i^*a_i=1$. The method of Lagrange multipliers instructs us to minimize

$$F(a_i^*,a_i)=\sum_{ij}a_i^*H_{ij}a_j-\lambda\sum_i a_i^*a_i$$

The condition is that $\partial F/\partial a_i^*=0$. The condition implies that

$$\sum_j H_{ij}a_j=\lambda a_i$$

Similarly $\partial F/\partial a_i=0$ implies that

$$\sum_i a_i^*H_{ij}=\lambda a_j^*$$

Thus the minimization condition yields solutions of an eigenvalue equation for H.

6. Consider the expectation value of *H* evaluated with the normalized trial wave function

$$\psi(x) = \left(\frac{\beta}{\sqrt{\pi}}\right)^{1/2} e^{-\beta^2 x^2/2}$$

Then an evaluation of the expectation value of *H* yields, after some algebra,

$$\begin{aligned} E(\beta) &= \int_{-\infty}^{\infty} dx\,\psi^*(x)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\psi(x) \\ &= \frac{\beta}{\sqrt{\pi}}\int_{-\infty}^{\infty} dx\left(\frac{\hbar^2}{2m}(\beta^2 - \beta^4 x^2)e^{-\beta^2 x^2}\right) + \frac{\beta}{\sqrt{\pi}}\int_{-\infty}^{\infty} dx\,V(x)e^{-\beta^2 x^2} \\ &= \frac{\hbar^2\beta^2}{2m} + \frac{\beta}{\sqrt{\pi}}\int_{-\infty}^{\infty} dx\,V(x)e^{-\beta^2 x^2} \end{aligned}$$

The question is: can we find a value of β such that this is negative. If so, then the true value of the ground state energy will necessarily be more negative. We are given the fact that the potential is attractive, that is, $V(x)$ is never positive. We write $V(x) = -|V(x)|$ and ask whether we can find a value of β such that

$$\frac{\beta}{\sqrt{\pi}}\int_{-\infty}^{\infty} dx\,|V(x)|\,e^{-\beta^2 x^2} > \frac{\hbar^2\beta^2}{2m}$$

For any given $|V(x)|$ we can always find a square "barrier" that is contained in the positive form of $|V(x)|$. If the height of that barrier is V_0 and it extends from $-a$ to $+a$, for example, then the left side of the above equation is always *larger than*

$$L(\beta) = \frac{\beta}{\sqrt{\pi}} V_0 \int_{-a}^{a} dx e^{-\beta^2 x^2}$$

Our question becomes: Can we find a β such that

$$\frac{4m}{\hbar^2} L(\beta) > \beta^2$$

It is clear that for small β such that $\beta^2 a^2 << 1$, the left hand side is approximated by $2a\frac{\beta}{\sqrt{\pi}}\frac{4mV_0}{\hbar^2}$. This is linear in β so that we can always find a β small enough so that the left hand side is larger than the right hand side.

7. The data indicates a resonance corresponding to a wavelength of 20.61 nm. This corresponds to an energy of

$$h\frac{c}{\lambda}=\frac{2\pi(1.054\times10^{-34}Js)(3\times10^{8}m/s)}{(20.61\times10^{-9}m)(1.602\times10^{-19}J/eV)}=60.17eV$$

above the ground state. The ground state has energy – 78.98 eV, while the ground state of He^+ has a binding energy of a hydrogenlike atom with $Z = 2$, that is, 54.42 eV. This means that the ionization energy of He is (78.98-54.42)eV = 24.55 eV above the ground state. Thus when the (2s)(2p) state decays into He^+ and an electron, the electron has an energy of (60.17 – 24.55)eV = 35.62 eV. This translates into
$v=\sqrt{2E/m}=3.54\times10^{6}m/s$.
The first excited state of the He^+ ion lies 54.42(1-1/4)=40.82 eV above the ground state of He^+ , and this is *above* the (2s)(2p) state.

8. To calculate the minimum of

$$E(\alpha_1,\alpha_2,...)=\frac{\langle\psi(\alpha_1,\alpha_2,...)|H|\psi(\alpha_1,\alpha_2,...)\rangle}{\langle\psi(\alpha_1,\alpha_2,...)|\psi(\alpha_1,\alpha_2,...)\rangle}$$

we set $\partial E/\partial\alpha_i=0,\ \ i=1,2,3....$ This implies that

$$\frac{\langle\frac{\partial\psi}{\partial\alpha_i}|H|\psi\rangle+\langle\psi|H|\frac{\partial\psi}{\partial\alpha_i}\rangle}{\langle\psi|\psi\rangle}-\frac{\langle\psi|H|\psi\rangle\left(\langle\frac{\partial\psi}{\partial\alpha_i}|\psi\rangle+\langle\psi|\frac{\partial\psi}{\partial\alpha_i}\rangle\right)}{\langle\psi|\psi\rangle^2}=0$$

This is equivalent to

$$\langle\frac{\partial\psi}{\partial\alpha_i}|H|\psi\rangle+\langle\psi|H|\frac{\partial\psi}{\partial\alpha_i}\rangle=$$
$$E(\alpha_1,\alpha_2,..)\left(\langle\frac{\partial\psi}{\partial\alpha_i}|\psi\rangle+\langle\psi|\frac{\partial\psi}{\partial\alpha_i}\rangle\right)$$

Let us now assume that *H* depends on some parameter λ.. To calculate the minimum we must choose our parameters α_i to depend on λ_i. We may rewrite the starting equation by emphasizing the dependence of everything on λ, as follows

$$E(\lambda)\langle\psi(\lambda)|\psi(\lambda)\rangle=\langle\psi(\lambda)|H|\psi(\lambda)\rangle$$

Let us now differentiate with respect to λ , noting that $\frac{\partial}{\partial\lambda}=\sum_i\frac{\partial\alpha_i}{\partial\lambda}\frac{\partial}{\partial\alpha_i}$

We get

$$\frac{dE(\lambda)}{d\lambda}\langle\psi(\lambda)\,|\,\psi(\lambda)\rangle + E(\lambda)\sum_i \frac{\partial\alpha_i}{\partial\lambda}\left(\langle\frac{\partial\psi}{\partial\alpha_i}\,|\,\psi(\lambda)\rangle + \langle\psi(\lambda)\,|\,\frac{\partial\psi(\lambda)}{\partial\alpha_i}\rangle\right) =$$

$$= \langle\psi(\lambda)\,|\,\frac{\partial H}{\partial\lambda}\,|\,\psi(\lambda)\rangle + \sum_i \frac{\partial\alpha_i}{\partial\lambda}\left(\langle\frac{\partial\psi}{\partial\alpha_i}\,|\,H\,|\,\psi(\lambda)\rangle + \langle\psi(\lambda)\,|\,H\,|\,\frac{\partial\psi(\lambda)}{\partial\alpha_i}\rangle\right)$$

Since we have shown that

$$\langle\frac{\partial\psi}{\partial\alpha_i}\,|\,H\,|\,\psi\rangle + \langle\psi\,|\,H\,|\,\frac{\partial\psi}{\partial\alpha_i}\rangle =$$

$$E(\alpha_1,\alpha_2,..)\left(\langle\frac{\partial\psi}{\partial\alpha_i}\,|\,\psi\rangle + \langle\psi\,|\,\frac{\partial\psi}{\partial\alpha_i}\rangle\right)$$

we obtain the result that

$$\frac{dE(\lambda)}{d\lambda}\langle\psi(\lambda)\,|\,\psi(\lambda)\rangle = \langle\psi(\lambda)\,|\,\frac{\partial H}{\partial\lambda}\,\psi(\lambda)\rangle$$

With normalized trial wave functions we end up with

$$\frac{dE(\lambda)}{d\lambda} = \langle\psi(\alpha_1,\alpha_2,..)\,|\,\frac{\partial H}{\partial\lambda}\,|\,\psi(\alpha_1,\alpha_2,..)\rangle$$

A comment: The Pauli theorem in Supplement 8-A has the same form, but it deals with exact eigenvalues and exact wave functions. Here we find that the same form applies to approximate values of the eigenvalue and eigenfunctions, provided that these are chosen to depend on parameters $\{\alpha\}$ which minimize the expectation value of the Hamiltonian (which does not depend on these parameters).

9. With the trial wave function

$$\psi(x) = \left(\frac{\beta}{\sqrt{\pi}}\right)^{1/2} e^{-\beta^2 x^2/2}$$

we can calculate

$$
\begin{aligned}
E(\beta) &= \frac{\beta}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx e^{-\beta^2 x^2/2} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \lambda x^4 \right) e^{-\beta^2 x^2/2} \\
&= \frac{\beta}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx e^{-\beta^2 x^2} \left(\frac{\hbar^2}{2m} (\beta^2 - \beta^4 x^2) + \lambda x^4 \right) \\
&= \frac{\hbar^2 \beta^2}{2m} + \frac{3\lambda}{4\beta^4}
\end{aligned}
$$

We minimize this by setting $\partial E / \partial \beta = 0$, which leads to $\beta^2 = \left(\frac{6m\lambda}{\hbar^2} \right)^{1/3}$. When this is inserted into the expression for *E*, we get

$$
E_{min} = \left(\frac{\hbar^2}{2m} \right)^{2/3} (4\lambda)^{1/3} \left(\frac{6^{1/3}}{4} + \frac{3}{4} \frac{1}{6^{2/3}} \right) = 1.083 \left(\frac{\hbar^2}{2m} \right)^{2/3} \lambda^{1/3}
$$

This is quite close to the exact value, for which the coefficient is 1.060

10. With the Hamiltonian

$$
H = \frac{p^2}{2m} + \lambda x^4
$$

we first choose (1/2*m*) as the parameter in the Feynman-Hellmann theorem. This leads to

$$
\langle 0 | p^2 | 0 \rangle = \frac{\partial E_{min}}{\partial (1/m)} = 0.890 (\hbar^4 m \lambda)^{1/3}
$$

If we choose λ as the parameter, then

$$
\langle 0 | x^4 | 0 \rangle = \frac{\partial E_{min}}{\partial \lambda} = 0.353 \left(\frac{\hbar^2}{2m\lambda} \right)^{2/3}
$$

11. We start from

$$
E_0 \leq \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\sum_{ij} a_i^* H_{ij} a_j}{\sum_i a_i^* a_i}
$$

We now choose for the trial vector one in which all the entries are zero, except that at the *k*-th position there is 1, so that $a_i = \delta_{ik}$. This leads to

$$E_0 \le H_{kk} \qquad (k \text{ is } \textit{not} \text{ summed over})$$

We may choose $k = 1,2,3,\ldots$ Thus the lowest eigenvalue is always smaller than the the smallest of the diagonal elements.

12. With the system's center of mass at rest, the two-body problem reduces to a one-body problem, whose Hamiltonian is

$$H = \frac{\mathbf{p}^2}{2\mu} + \frac{1}{2}\mu\omega^2 r^2$$

where μ is the reduced mass, whose value is $m/2$.

(**a**) The two particles are in an $l = 0$ state which means that the ground state wave function only depends on r, which is symmetric under the interchange of the two particles (Recall that $r = |\mathbf{r}_1 - \mathbf{r}_2|$). Thus the electrons must be in a spin-singlet state, and the ground state wave function is

$$\psi(\mathbf{r}) = u_0(r) X_{singlet}$$

where

$$u_0(r) = u_0(x)u_0(y)u_0(z) = \left(\frac{\mu\omega}{\hbar\pi}\right)^{3/4} e^{-\mu\omega r^2/2\hbar}$$

(We use $u_0(x)$ from Eq. (6-55)).

(b) To proceed with this we actually have to know something about the solutions of the simple harmonic oscillator in three dimensions. The solution of this was required by Problem 13 in Chapter 8. We recall that the solutions are very similar to the hydrogen atom problem. There are two quantum numbers, n_r and l. Here $l = 0$, so that the first excited *singlet* state must correspond to $n_r = 1$. In the spin triplet state, the spin-wave function is symmetric, so that the spatial wave function must be *antisymmetric*. This is not possible with $l = 0$!

To actually obtain the wave function for the first excited singlet state, we look at the equation for $H(\rho)$, with $H(\rho)$ of the form $a + b\rho^2$. Since

$$\frac{d^2H}{d\rho^2} + 2\left(\frac{1}{\rho} - \rho\right)\frac{dH}{d\rho} + 4H = 0$$

We get $H(\rho) = 1 - 2\rho^2/3$ and the solution is

$$u_1(r) = N\left(1 - \frac{2}{3}\rho^2\right)e^{-\rho^2/2}$$

where $\rho = \left(\frac{\mu\omega}{\hbar}\right)^{1/2} r$. The normalization constant is obtained from the requirement that

$$N^2 \int_0^\infty r^2 dr (1 - \frac{2\mu\omega}{3\hbar} r^2)^2 e^{-\mu\omega r^2/\hbar} = 1$$

so that

$$N^2 = \frac{6}{\sqrt{\pi}} \left(\frac{\mu\omega}{\hbar}\right)^{3/2}$$

(c) The energy shift to lowest order is

$$\Delta E = \int_0^\infty r^2 dr \left[C \frac{\delta(r)}{r^2} \right] N^2 (1 - \frac{2\mu\omega}{3\hbar} r^2)^2 e^{-\mu\omega r^2/\hbar} = CN^2$$

13. The energy is given by

$$E = \frac{1}{2} M_{red} \omega^2 (R - R_0)^2 + \frac{\hbar^2 J(J+1)}{2 M_{red} R^2}$$

If we treat the vibrational potential classically, then the lowest state of energy is characterized by $R = R_0$. The vibrational motion changes the separation of the nuclei in the molecule. The new equilibrium point is given by R_1, which is determined by the solution of

$$\left(\frac{\partial E}{\partial R}\right)_{R_1} = 0 = M_{red} \omega^2 (R_1 - R_0) - \frac{J(J+1)\hbar^2}{M_{red} R_1^3}$$

Let $R_1 = R_0 + \Delta$. Then to first order in Δ,

$$\Delta = \frac{J(J+1)\hbar^2}{M_{red}^2 \omega^2 R_0^3}$$

If we now insert the new value of R_1 into the energy equation, we find that only the rotational energy is changed (since the vibrational part is proportional to Δ^2). The rotational energy is now

$$E_{rot} = \frac{J(J+1)\hbar^2}{2 M_{red} R_0^2 (1 + 2\Delta / R_0)}$$

$$= \frac{J(J+1)\hbar^2}{2 M_{red} R_0^2} - (J(J+1))^2 \frac{\hbar^4}{M_{red}^3 \omega^2 R_0^6}$$

The sign of the second term is negative. The sign is dictated by the fact that the rotation stretches the molecule and effectively increases its moment of inertia.

14. In the transition $J = 1$ → $J = 0$ we have

$$\Delta E = \frac{\hbar^2}{2M_{red}R^2}(2-0) = \frac{2\pi\hbar c}{\lambda}$$

so that

$$R^2 = \frac{\hbar\lambda}{2\pi c}\frac{1}{M_{red}} = \frac{\hbar\lambda}{2\pi c}\frac{1}{M_{nucleon}}\left(\frac{1}{12}+\frac{1}{16}\right) =$$
$$= (1.127\times 10^{-10}\,m)^2$$

The internuclear separation is therefore 0.113 nm, and the momentu of inertia is

$$M_{red}R^2 = 1.45\times 10^{-46}\,kg.m^2$$

15. (a) The two nuclei are identical. Since the two-electron state is a spatially symmetric spin 0 state, we can ignore the electrons in discussing the lowest energy states of the molecule. In the ground state, the two protons will be in the symmetric $L = 0$ state, so that they must be in a spin-antisymmetric $S = 0$ state.

For the spin-symmetric $S = 1$ state, the spatial wave function must be antisymmetric, so that the lowest energy state will have $L = 1$.

(**b**) The lowest energy state that lies above the ground state of $L = 0$, and is also a spin $S = 0$ state must have $L = 2$. Thus the change in energy in the transition is

$$\Delta E = \frac{\hbar^2}{M_pR^2}\left(2(2+1)-0\right) = \frac{6\hbar^2}{M_pR^2} = \frac{2\pi\hbar c}{\lambda_s}$$

We have used the fact that the reduced mass of the two-proton system is $M_p/2$.

For the $S = 1$ system, the state above the lowest $L = 1$ state is the $L = 3$ state, and here

$$\Delta E = \frac{\hbar^2}{M_pR^2}\left(3(3+1)-1(1+1)\right) = \frac{10\hbar^2}{M_pR^2} = \frac{2\pi\hbar c}{\lambda_t}$$

The singlet and triplet wavelengths are easily calculated once we know R. Note that these are not exactly the same, but can be looked up.