Homework II, solutions

Problem 1, solution

a) The Schrödinger equation is

\[ \left[ \frac{\hbar^2}{2M} \frac{\partial^2}{\partial r^2} + V(r) - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \theta^2} \right] \Phi(r, \theta) \chi(\phi) = E \Phi(r, \theta) \chi(\phi) \]

Here \( H_c \) is the CM motion, \( H_{rad} \) is the relative motion, and \( H_{spin} \) is the spin.

\[ H = H_c + H_{rad} + H_{spin} \]

\[ [H_{rad}, H_{spin}] = 0 \]

\[ V_B = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \theta^2} \]

In the basis \( \{ \| \uparrow \rangle, \| \downarrow \rangle, \| \uparrow \downarrow \rangle, \| \downarrow \uparrow \rangle \} \), the matrix of \( V_B \) is:

\[
(V_B) = \begin{pmatrix}
\langle \uparrow | V_B | \uparrow \rangle & 0 & 0 & 0 \\
\langle \downarrow | V_B | \uparrow \rangle & 0 & 0 & 0 \\
\langle \uparrow | V_B | \downarrow \rangle & 0 & 0 & -V(r) \\
\langle \downarrow | V_B | \downarrow \rangle & 0 & 0 & -V(r)
\end{pmatrix}
\]

The eigenfunctions are

\[ \langle \uparrow | V_B | \uparrow \rangle, \langle \downarrow | V_B | \uparrow \rangle, \langle \uparrow | V_B | \downarrow \rangle, \langle \downarrow | V_B | \downarrow \rangle \]

with eigenvalues \( -V(r) \) and \( \frac{\hbar^2}{12} \langle \downarrow | \downarrow \rangle \) with eigenvalue \( V(r) \).

The symmetric eigenfunction (triplet state) is lower in energy.

\[ \langle V_B \rangle_s = -V(r), \quad \langle V_B \rangle_A = V(r) \]

so the ground state is the triplet state.

b) If both particles had the same \( \frac{1}{2} \) component, the state vector in the spin space would have to be symmetric. (We would have identical particles.) The ground state is symmetric in orbital space, so we need the state vector in spin space to be antisymmetric. This implies higher energy.
The two-electron wave function must be antisymmetric with respect to interchange of position and spin variables.

\[ S = 0 \Rightarrow \text{symmetric space wave function} \]
\[ S = 1 \Rightarrow \text{antisymmetric space wave function} \]

\[ S = 0: \quad \psi_S^{(p_1, p_2)} = \frac{\psi_0(p_1) \psi_0(p_2) + \psi_1(p_1) \psi_1(p_2)}{\sqrt{2}} \]
\[ S = 1: \quad \psi_T^{(p_1, p_2)} = \frac{\psi_S(p_1) \psi_S(p_2) - \psi_S(p_2) \psi_S(p_1)}{\sqrt{2}} \]

Set \[ H = H_0 + \frac{\alpha^2}{r_{12}} \] and treat \[ \frac{\alpha^2}{r_{12}} \] as a perturbation.

The unperturbed energies of \( \psi_S \) and \( \psi_T \) are equal. (\( \psi_S \) and \( \psi_T \) are eigenfunctions of \( H_0 \).) The first order corrections differ by

\[ \langle \psi_S \mid \frac{\alpha^2}{r_{12}} \mid \psi_T \rangle - \langle \psi_T \mid \frac{\alpha^2}{r_{12}} \mid \psi_T \rangle = 2 \langle \psi_S(p_1) \psi_S(p_2) \mid \frac{\alpha^2}{r_{12}} \mid \psi_S(p_2) \psi_S(p_1) \rangle \]

\[ = 2 \left( \frac{\alpha}{a_0} \right) \left( \frac{1}{4\pi a_0^2} \right) e^2 \int \frac{d^3 r_1 d^3 r_2}{(r_{12} - \infty)^2} \left( \frac{2}{a_0} - \frac{2\pi}{a_0} \right) \frac{e^{-2(r_{12})/a_0}}{r_{12}} = \Delta \]

\[ \frac{1}{r_{12}^2} = \sum \frac{Z e^2}{2\pi \hbar c} \sum \frac{1}{m+e} Y_{em}(\theta \phi) Y_{em}^*(\theta \phi) \]

\[ e^{-2(r_{12})/a_0} \]

is invariant under separate rotations of \( r_1 \) and \( r_2 \). Therefore only \( \ell = 0 \) term survives the angular integration. We have

\[ \Delta = 2 (4\pi)^2 \left( \frac{\alpha}{a_0} \right) \left( \frac{1}{4\pi a_0^2} \right) e^2 \int_{r_{12} > 0} r_1^2 r_2^2 (2\cdot \frac{2\pi}{a_0})^2 e^{-2(r_{12})/a_0} \left( \frac{2}{a_0} - \frac{2\pi}{a_0} \right) \frac{e^{-2(r_{12})/a_0}}{r_{12}} \]

\[ = \frac{64 e^2}{a_0^6} \int_{r_{12} > 0} r_1^2 r_2^2 \frac{e^{-2(r_{12})/a_0}}{r_{12}} \int_{r_{12} > 0} r_1^2 r_2^2 \frac{e^{-2(r_{12})/a_0}}{r_{12}} \frac{e^{-2(r_{12})/a_0}}{r_{12}} = \frac{64}{729} \frac{e^2}{a_0} = 2.89 \text{ eV} \]

(All integrals are in the table.)
Problem 3: Solution

\[ H = \frac{P_r^2}{2m} + \frac{B_r^2}{2m} + \frac{1}{2} C x_1^2 + \frac{1}{2} C x_2^2 + \frac{1}{2} k (x_1 - x_2)^2. \]

a) \( R = \frac{1}{2} (x_1 + x_2), \ r = (x_2 - x_1), \ x_1 = R - \frac{1}{2} r, \ x_2 = R + \frac{1}{2} r. \)

\[ L = T - V = \frac{1}{2} m (\dot{x}_1^2 + \dot{x}_2^2) - V = \frac{1}{2} (mR^2 + m r^2) - V \quad \text{where} \quad m = 2m \quad \text{and} \quad u = \frac{m}{2}. \]

\[ \rho_R = \frac{\partial L}{\partial R} = m \dot{R}, \ \rho_r = \frac{\partial L}{\partial r} = m \dot{r}, \ H = \frac{P_R^2}{2m} + \frac{P_r^2}{2m} + V. \]

We want \( V = \frac{1}{2} C x_1^2 + \frac{1}{2} C x_2^2 + \frac{1}{2} x_1 x_2^2 + \frac{1}{2} k x_1^2 - k x_1 x_2 = \frac{1}{2} A R^2 + \frac{1}{2} B \quad \text{for} \quad R = \frac{1}{2} (x_1 + x_2) + \frac{1}{2} B (x_1^2 + x_2^2 - 2 x_1 x_2). \)

Therefore \( \frac{1}{2} (C + k) = \frac{1}{2} (\frac{A}{2} + B), \ -k = \frac{1}{2} A - B, \ \text{or} \quad A = 2C, \ B = \frac{C}{2} + k. \)

\[ H = \frac{P_R^2}{2m} + \frac{1}{2} A R^2 + \frac{P_r^2}{2m} + \frac{1}{2} B r^2. \]

To make the transition to Quantum Mechanics let \( P_R, P_r, R, \) and \( r \) become operators.

b) \( \text{Let} \quad x = \chi(R) \phi(r). \quad \text{Then} \)

\[ -\frac{1}{2m} \frac{\partial^2}{\partial R^2} \chi(R) + \frac{1}{2} A R^2 \chi(R) = E_1 \chi(R); \quad -\frac{k}{2m} \frac{\partial^2}{\partial r^2} \phi(r) + \frac{1}{2} B r^2 \phi(r) = E_2 \phi(r). \]

\[ E = E_1 + E_2, \quad E_1 = (n_1 + \frac{1}{2}) \hbar \omega_1, \quad E_2 = (n_2 + \frac{1}{2}) \hbar \omega_2. \quad \omega_1 = \frac{A}{M}, \quad \omega_2 = \frac{B}{M}. \]

\( n_1 = 0, 1, 2, \ldots; \quad n_2 = 0, 1, 2, \ldots. \)

c) For indistinguishable bosons the total wavefunction must be symmetric under interchange of the two particles, for indistinguishable fermions it must be antisymmetric.

Under interchange \( R \rightarrow R_1, \ r \rightarrow - r. \ \phi_{n_2}(r) \) has even parity if \( n_2 \) is even and odd parity if \( n_2 \) is odd.

To get an even space function we need \( n_2 \) even, to get an odd space function we need \( n_2 \) odd.

If the spin function is symmetric, then we have \( E = E_{n_1} + E_{n_2}, \ n_2 \) even for bosons and \( E = E_{n_1} + E_{n_2}, \ n_2 \) odd for fermions.

d) \( \phi_{n_2}(0) = 0 \) if \( n_2 \) odd. \( \Gamma \rightarrow \pi \rightarrow x = x_2 \rightarrow \phi_{n_2} \text{odd}. \)