

Prelim Solutions: J18

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1 Q.1

Here, we use $\psi_{nlm}^{(1)}$ to indicate a wavefunction centered on atom 1 and $\psi_{nlm}^{(2)}$ for atom 2. Let the position of the two hydrogen atoms be \mathbf{R}_1 and \mathbf{R}_2 each. The quantity:

$$\int d^3r_1 \psi_{nlm}^{(1)}(\mathbf{r}_1 - \mathbf{R}_1) \psi_{nlm}^{(2)*}(\mathbf{r}_1 - \mathbf{R}_2) \approx e^{-R/a_0} \quad (1)$$

where R is the distance between the two atoms. This is thus exponentially suppressed and we only consider overlaps between states on the same atom to be non-zero.

1.1 a.

The leading ground state wave function is:

$$\psi_{gs}(r_1, r_2) = \frac{1}{\sqrt{2}} (\psi_{100}^{(1)}(r_1) \psi_{100}^{(2)}(r_2) + \psi_{100}^{(2)}(r_1) \psi_{100}^{(1)}(r_2)) \times \frac{1}{\sqrt{2}} (|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2) \quad (2)$$

where we have symmetrized the wavefunctions since the total spin $S = 0$ configurations imply that the spin part of the wavefunction is antisymmetric (and thus the total wavefunction is antisymmetric). The leading order ground state energy is $-2E_b$ where E_b is the binding energy of one hydrogen atom (13.6eV).

1.2 b.

The perturbing Hamiltonian is of the form:

$$U_{dipole} = \frac{e^2}{4\pi\epsilon_0 R^3} (\vec{r}_1 \cdot \vec{r}_2 - 3r_{1z}r_{2z}) \quad (3)$$

The first order corrections to this Hamiltonian is the form:

$$E^{(1)} \propto \langle \psi_{100}^{(1)} | r_1 | \psi_{100}^{(1)} \rangle = 0 \quad (4)$$

Thus, this Hamiltonian only receives corrections at the second order. Hence, $\delta_0 = 6$. The overlap with the 2p orbital (and other parity odd orbitals) gives a non-zero second order contribution.

1.3 c.

The sign of A_0 is negative since this is the second order contribution to the ground state.

$$A_0 \approx -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{|\langle \psi_{210} | r | \psi_{100} \rangle|^4}{E_2 - E_1} \approx -\left(\frac{e^2 a_0^2}{4\pi\epsilon_0}\right)^2 \frac{1}{E_b} \quad (5)$$

where we take the second order contribution from the 2p orbital overlap as the leading order contribution and use a_0 as an effective contribution for the overlap of the \mathbf{r} operator and use the binding energy of the Hydrogen atom as an estimate for the energy gap between levels.

1.4 d.

In this case, the unperturbed ground state would involve 1s on one atom and 2s or 2p on the other. Thus, this is degenerate. The Hamiltonian perturbation breaks this degeneracy. To first order, the state involving 1s and 2s has no contribution since both are parity even. Additionally,

$$\vec{d}^1 \cdot \vec{d}^2 - 3d_z^1 d_z^2 = d_x^1 d_x^2 + d_y^1 d_y^2 - 2d_z^1 d_z^2 \quad (6)$$

The z direction terms effectively reduce the energy in the z direction compared to the other directions. (The term before that is rotationally invariant).

Therefore, our first excited state involves the $2p_z$ orbital.

$$\psi_{ex}(r_1, r_2) = \frac{1}{2}(\psi_{210}^{(1)}(r_1)\psi_{100}^{(2)}(r_2) + \psi_{100}^{(2)}(r_1)\psi_{210}^{(1)}(r_2) + \psi_{210}^{(2)}(r_1)\psi_{100}^{(1)}(r_2) + \psi_{100}^{(1)}(r_1)\psi_{210}^{(2)}(r_2)) \quad (7)$$

The symmetrization between the two atoms gives a net lowering in energy.

$\delta_1 = 3$ since we have a first order contribution of the order

$$A_1 \approx -\left(\frac{e^2 a_0^2}{4\pi\epsilon_0}\right) \quad (8)$$

where we have a lower of energy.