

Assignment 2Q.1

Soln Water molecule consists of two H atoms (H_1, H_2) and one O atom (O).

Let's denote nuclei of H_1 with I, nuclei of H_2 with J and nuclei of O with K.

Let's denote all the electrons with i .

$$\begin{aligned}\hat{H}_{H_2O} = & -\frac{1}{2} \sum_i \nabla_i^2 - \sum_I \frac{1}{2M_I} \nabla_I^2 - \sum_J \frac{1}{2M_J} \nabla_J^2 \\ & - \sum_K \frac{1}{2M_K} \nabla_K^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|} + \frac{1}{2} \sum_{J \neq K} \frac{Z_J Z_K}{|R_J - R_K|} \\ & + \frac{1}{2} \sum_{I \neq K} \frac{Z_I Z_K}{|R_I - R_K|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} \\ & - \sum_{i, I} \frac{Z_I}{|r_i - R_I|} - \sum_{i, J} \frac{Z_J}{|r_i - R_J|} - \sum_{i, K} \frac{Z_K}{|r_i - R_K|}\end{aligned}$$

Apply clamped ion approximation and substitute

$$Z_I = 1, \quad Z_J = 1, \quad Z_K = 8$$

$$\begin{aligned}\hat{H}_{H_2O} = & -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} - \sum_{i, I} \frac{1}{|r_i - R_I|} \\ & - \sum_{i, J} \frac{1}{|r_i - R_J|} - \sum_{i, K} \frac{8}{|r_i - R_K|}\end{aligned}$$

Q.3

Soln

He atom

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(x_1) & \psi_2(x_2) \\ \psi_2(x_1) & \psi_1(x_2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} (\psi_1(x_1) \psi_1(x_2) - \psi_2(x_1) \psi_2(x_2))$$

$$n(x_1) = 2 \int |\Psi(x_1, x_2)|^2 dx_2$$

$$= 2 \int \Psi(x_1, x_2) \Psi^*(x_1, x_2) dx_2$$

$$= 2 \cdot \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}} \int (\psi_1(x_1) \psi_1(x_2) - \psi_2(x_1) \psi_2(x_2)) (\psi_1^*(x_1) \psi_1^*(x_2) - \psi_2^*(x_1) \psi_2^*(x_2)) dx_2$$

$$= \int (|\psi_1(x_1)|^2 |\psi_1(x_2)|^2 + |\psi_2(x_1)|^2 |\psi_2(x_2)|^2 - \psi_1^*(x_1) \psi_2(x_1) \psi_1^*(x_2) \psi_2(x_2) - \psi_1(x_1) \psi_2^*(x_1) \psi_1(x_2) \psi_2^*(x_2)) dx_2$$

$$= |\psi_1(x_1)|^2 \int |\psi_1(x_2)|^2 dx_2 + |\psi_2(x_1)|^2 \int |\psi_2(x_2)|^2 dx_2$$

$$- \psi_1^*(x_1) \psi_2(x_1) \int \psi_1^*(x_2) \psi_2(x_2) dx_2$$

$$- \psi_1(x_1) \psi_2^*(x_1) \int \psi_1(x_2) \psi_2^*(x_2) dx_2$$

Using $\int \psi_1^*(x_1) \psi_2(x_1) dx_1 = 0$

Also, $\int \psi_1(x_1) \psi_2^*(x_1) dx_1 = 0$

Since $|\Psi(x_1)|^2$ is gradual probability density, its integral over x_1 will be equal to 1

Date.....

$$2) \quad n(x) = |\psi_1(x)|^2 \times 1 + |\psi_2(x)|^2 \times 1 - 0 - 0$$

$$3) \quad \boxed{n(x) = |\psi_1(x)|^2 + |\psi_2(x)|^2}$$