

Chapter 6. Diatomic molecules



Total Hamiltonian: $\hat{H} = \hat{H}_n + \hat{H}_e$

Nuclear term: $\hat{H}_n = \frac{\hat{\mathbf{p}}_A^2}{2m_A} + \frac{\hat{\mathbf{p}}_B^2}{2m_B} + \frac{Z_A Z_B e^2}{|\hat{\mathbf{r}}_A - \hat{\mathbf{r}}_B|}$,

Electron term: $\hat{H}_e = \sum_{i=1}^N \left\{ \frac{\hat{\mathbf{p}}_i^2}{2m_e} - \frac{Z_A e^2}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_A|} - \frac{Z_B e^2}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_B|} \right\} + \sum_{i>j}^N \frac{e^2}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|}$

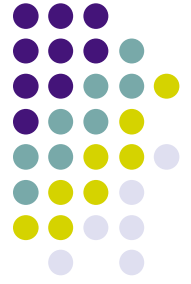
Nuclear position (operators)

Nuclear position state: $|\mathbf{R}\rangle = |\mathbf{r}_A\rangle \otimes |\mathbf{r}_B\rangle = |\mathbf{r}_A, \mathbf{r}_B\rangle$

$\hat{H}_e |\mathbf{R}\rangle = \hat{H}_{en}(\mathbf{R}) |\mathbf{R}\rangle$ Specification (measurement) nuclear coordinate

$$\hat{H}_{en}(\mathbf{R}) = \sum_{i=1}^N \left\{ \frac{\hat{\mathbf{p}}_i^2}{2m_e} - \frac{Z_A e^2}{|\hat{\mathbf{r}}_i - \mathbf{r}_A|} - \frac{Z_B e^2}{|\hat{\mathbf{r}}_i - \mathbf{r}_B|} \right\} + \sum_{i>j}^N \frac{e^2}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|}$$

Nuclear position (parameters)



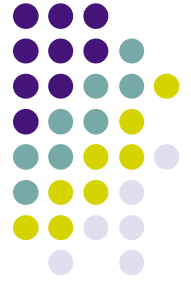
Electronic eigenstate and eigenvalue (depending on nuclear coordinates as parameters).

$$\hat{H}_{en}(\mathbf{R})|E_k(\mathbf{R})\rangle = E_k(\mathbf{R})|E_k(\mathbf{R})\rangle$$

$$\langle \mathbf{R}|E_T\rangle = \psi_{N,k}(\mathbf{R})|E_k(\mathbf{R})\rangle$$

$$\begin{aligned} E_T \langle \mathbf{R}|E_T\rangle &= \langle \mathbf{R}|(\hat{H}_n + \hat{H}_e)|E_T\rangle = \langle \mathbf{R}|\hat{H}_n|E_T\rangle + \hat{H}_{en}(\mathbf{R})\langle \mathbf{R}|E_T\rangle \\ &= \left(-\frac{\hbar^2}{2m_A} \nabla_A^2 - \frac{\hbar^2}{2m_B} \nabla_B^2 + \frac{Z_A Z_B e^2}{|\mathbf{r}_A - \mathbf{r}_B|} + \hat{H}_{en}(\mathbf{R}) \right) \langle \mathbf{R}|E_T\rangle \\ &= \left(-\frac{\hbar^2}{2m_A} \nabla_A^2 - \frac{\hbar^2}{2m_B} \nabla_B^2 + \frac{Z_A Z_B e^2}{|\mathbf{r}_A - \mathbf{r}_B|} + E_k(\mathbf{R}) \right) \psi_{N,k}(\mathbf{R})|E_k(\mathbf{R})\rangle \end{aligned}$$

$$\begin{aligned} \nabla_{A(B)}^2 \{ \psi_{N,k}(\mathbf{R})|E_k(\mathbf{R})\rangle \} &= \left\{ \nabla_{A(B)}^2 \psi_{N,k}(\mathbf{R}) \right\} |E_k(\mathbf{R})\rangle \\ &+ 2 \left\{ \nabla_{A(B)} \psi_{N,k}(\mathbf{R}) \right\} \cdot \left\{ \nabla_{A(B)} |E_k(\mathbf{R})\rangle \right\} \\ &+ \psi_{N,k}(\mathbf{R}) \left\{ \nabla_{A(B)}^2 |E_k(\mathbf{R})\rangle \right\} \end{aligned}$$



Born-Oppenheimer Approximation:

$$\nabla_{A(B)}^2 \{ \psi_{N,k}(\mathbf{R}) |E_k(\mathbf{R})\rangle \} \approx |E_k(\mathbf{R})\rangle \nabla_{A(B)}^2 \psi_{N,k}(\mathbf{R})$$

$$\begin{aligned} |E_k(\mathbf{R})\rangle \left\{ -\frac{\hbar^2}{2m_A} \nabla_A^2 - \frac{\hbar^2}{2m_B} \nabla_B^2 + \frac{Z_A Z_B e^2}{|\mathbf{r}_A - \mathbf{r}_B|} + E_i(\mathbf{R}) \right\} \psi_{N,k}(\mathbf{R}) \\ = E_T |E_k(\mathbf{R})\rangle \psi_{N,k}(\mathbf{R}) \end{aligned}$$

Inner product with $\langle E_k(\mathbf{R})|$.

$$\text{Born-Oppenheimer potential energy surface: } U_k(\mathbf{R}) = \frac{Z_A Z_B e^2}{|\mathbf{r}_A - \mathbf{r}_B|} + E_k(\mathbf{R})$$

Schrodinger Eqn. for nuclear degrees of freedom:

$$\left\{ -\frac{\hbar^2}{2m_A} \nabla_A^2 - \frac{\hbar^2}{2m_B} \nabla_B^2 + U_k(\mathbf{R}) \right\} \psi_{N,k}(\mathbf{R}) = E_T \psi_{N,k}(\mathbf{R})$$

