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).

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

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

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

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

Born-Oppenheimer Approximation:

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

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

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

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:

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