

## 26.1: The Molecular Hamiltonian

For a molecule, we can decompose the Hamiltonian operator as:

$$\hat{H} = \hat{K}_N + \hat{K}_e + \hat{V}_{NN} + \hat{V}_{eN} + \hat{K}_{ee} \quad (26.1.1)$$

where we have decomposed the kinetic energy operator into nuclear and electronic terms,  $\hat{K}_N$  and  $\hat{K}_e$ , as well as the potential energy operator into terms representing the interactions between nuclei,  $\hat{V}_{NN}$ , between electrons,  $\hat{V}_{ee}$ , and between electrons and nuclei,  $\hat{V}_{eN}$ . Each term can then be calculated using:

$$\begin{aligned} \hat{K}_N &= - \sum_i^{\text{nuclei}} \frac{\hbar^2}{2M_i} \nabla_{\mathbf{R}_i}^2 \\ \hat{K}_e &= - \sum_i^{\text{electrons}} \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 \\ \hat{V}_{NN} &= \sum_i \sum_{j>i} \frac{Z_i Z_j e^2}{4\pi\epsilon_0 |\mathbf{R}_i - \mathbf{R}_j|} \\ \hat{V}_{eN} &= - \sum_i \sum_j \frac{Z_i e^2}{4\pi\epsilon_0 |\mathbf{R}_i - \mathbf{r}_j|} \\ \hat{V}_{ee} &= \sum_i \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \end{aligned} \quad (26.1.2)$$

where  $M_i$ ,  $Z_i$ , and  $\mathbf{R}_i$  are the mass, atomic number, and coordinates of nucleus  $i$ , respectively, and all other symbols are the same as those used in [Equation 26.1](#) for the many-electron atom Hamiltonian.

### Small terms in the molecular Hamiltonian

The operator in [Equation 26.1.1](#) is known as the “exact” nonrelativistic Hamiltonian in field-free space. However, it is important to remember that it neglects at least two effects. Firstly, although the speed of an electron in a hydrogen atom is less than 1% of the speed of light, relativistic mass corrections can become appreciable for the inner electrons of heavier atoms. Secondly, we have neglected the spin-orbit effects, which is explained as follows. From the point of view of an electron, it is being orbited by a nucleus which produces a magnetic field (proportional to  $\mathbf{L}$ ); this field interacts with the electron’s magnetic moment (proportional to  $\mathbf{S}$ ), giving rise to a spin-orbit interaction (proportional to  $\mathbf{L} \cdot \mathbf{S}$  for a diatomic.) Although spin-orbit effects can be important, they are generally neglected in quantum chemical calculations, and we will neglect them in the remainder of this textbook as well.

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