

26.2: The Born-Oppenheimer Approximation

As we already saw in the previous chapter, if a Hamiltonian is separable into two or more terms, then the total eigenfunctions are products of the individual eigenfunctions of the separated Hamiltonian terms. The total eigenvalues are then sums of individual eigenvalues of the separated Hamiltonian terms.

For example, let's consider a Hamiltonian that is separable into two terms, one involving coordinate q_1 and the other involving coordinate q_2 :

$$\hat{H} = \hat{H}_1(q_1) + \hat{H}_2(q_2) \quad (26.2.1)$$

with the overall Schrödinger equation being:

$$\hat{H}\psi(q_1, q_2) = E\psi(q_1, q_2). \quad (26.2.2)$$

If we assume that the total wave function can be written in the form:

$$\psi(q_1, q_2) = \psi_1(q_1)\psi_2(q_2), \quad (26.2.3)$$

where $\psi_1(q_1)$ and $\psi_2(q_2)$ are eigenfunctions of \hat{H}_1 and \hat{H}_2 with eigenvalues E_1 and E_2 , then:

$$\begin{aligned} \hat{H}\psi(q_1, q_2) &= (\hat{H}_1 + \hat{H}_2)\psi_1(q_1)\psi_2(q_2) \\ &= \hat{H}_1\psi_1(q_1)\psi_2(q_2) + \hat{H}_2\psi_1(q_1)\psi_2(q_2) \\ &= E_1\psi_1(q_1)\psi_2(q_2) + E_2\psi_1(q_1)\psi_2(q_2) \\ &= (E_1 + E_2)\psi_1(q_1)\psi_2(q_2) \\ &= E\psi(q_1, q_2) \end{aligned} \quad (26.2.4)$$

Thus the eigenfunctions of \hat{H} are products of the eigenfunctions of \hat{H}_1 and \hat{H}_2 , and the eigenvalues are the sums of eigenvalues of \hat{H}_1 and \hat{H}_2 .

If we examine the nonrelativistic Hamiltonian in Equation 27.1.1, we see that the \hat{V}_{en} terms prevents us from cleanly separating the electronic and nuclear coordinates and writing the total wave function. If we neglect these terms, we can write the total wave function as:

$$\psi(\mathbf{r}, \mathbf{R}) = \psi_e(\mathbf{r})\psi_N(\mathbf{R}), \quad (26.2.5)$$

This approximation is called the **Born-Oppenheimer approximation**, and allows us to treat the nuclei as nearly fixed with respect to electron motion. The Born-Oppenheimer approximation is almost always quantitatively correct, since the nuclei are much heavier than the electrons and the (fast) motion of the latter does not affect the (slow) motion of the former. Using this approximation, we can fix the nuclear configuration at some value, \mathbf{R}_a , and solve for the electronic portion of the wave function, which is dependent only parametrically on \mathbf{R} (we write this wave function as $\psi_e(\mathbf{r}; \mathbf{R}_a)$, where the semicolon indicates the parametric dependence on the nuclear configuration). To solve the TISEq we can then write the electronic Hamiltonian as:

$$\hat{H}_e = \hat{K}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \mathbf{R}_a) + \hat{V}_{ee}(\mathbf{r}) \quad (26.2.6)$$

where we have also factored out the nuclear kinetic energy, \hat{K}_N (since it is smaller than \hat{K}_e by a factor of $\frac{M_i}{m_e}$), as well as $\hat{V}_{NN}(\mathbf{R})$. This latter approximation is justified, since in the Born-Oppenheimer approximation \mathbf{R} is just a parameter, and $\hat{V}_{NN}(\mathbf{R}_a)$ is a constant that shifts the eigenvalues only by some fixed amount. This electronic Hamiltonian results in the following TISEq:

$$\hat{H}_e\psi_e(\mathbf{r}; \mathbf{R}_a) = E_e\psi_e(\mathbf{r}; \mathbf{R}_a), \quad (26.2.7)$$

which is the equation that is used to explain the chemical bond in the next section. Notice that Equation 26.2.7 is not the total TISEq of the system, since the nuclear eigenfunction and its eigenvalues (which can be obtained solving the Schrödinger equation with the nuclear Hamiltonian) are neglected. As a final note, in the remainder of this textbook we will confuse the term “total energy” with “total energy at fixed geometry”, as is customary in many other quantum chemistry textbooks (i.e., we are neglecting the nuclear kinetic energy). This is just E_e of Equation 26.2.7, plus the constant shift, $\hat{V}_{NN}(\mathbf{R}_a)$, given by the nuclear-nuclear repulsion.

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