

### 3.1: The Born-Oppenheimer Separation of Electronic and Nuclear Motions

Many elements of chemists' pictures of molecular structure hinge on the point of view that separates the electronic motions from the vibrational/rotational motions and treats couplings between these (approximately) separated motions as 'perturbations'. It is essential to understand the origins and limitations of this separated-motions picture.

To develop a framework in terms of which to understand when such separability is valid, one thinks of an atom or molecule as consisting of a collection of  $N$  electrons and  $M$  nuclei each of which possesses kinetic energy and among which coulombic potential energies of interaction arise. To properly describe the motions of all these particles, one needs to consider the full Schrödinger equation  $H\Psi = E\Psi$ , in which the Hamiltonian  $H$  contains the sum (denoted  $H_e$ ) of the kinetic energies of all  $N$  electrons and the coulomb potential energies among the  $N$  electrons and the  $M$  nuclei as well as the kinetic energy  $T$  of the  $M$  nuclei

$$T = \sum_{a=1,M} \left( \frac{-\hbar^2}{2m_a} \right) \nabla_a^2,$$

$$H = H_e + T$$

$$H_e = \sum_j \left[ \frac{-\hbar^2}{2m_e} \nabla_j^2 - \sum_a \frac{Z_a e^2}{r_{j,a}} \right] + \sum_{j < k} \frac{e^2}{r_{j,k}} + \sum_{a < b} Z_a Z_b \frac{e^2}{R_{a,b}}.$$

Here,  $m_a$  is the mass of the nucleus  $a$ ,  $Z_a e^2$  is its charge, and  $\nabla_a^2$  is the Laplacian with respect to the three cartesian coordinates of this nucleus (this operator  $\nabla_a^2$  is given in spherical polar coordinates in Appendix A);  $r_{j,a}$  is the distance between the  $j^{\text{th}}$  electron and the  $a^{\text{th}}$  nucleus,  $r_{j,k}$  is the distance between the  $j^{\text{th}}$  and  $k^{\text{th}}$  electrons,  $m_e$  is the electron's mass, and  $R_{a,b}$  is the distance from nucleus  $a$  to nucleus  $b$ .

The full Hamiltonian  $H$  thus contains differential operators over the  $3N$  electronic coordinates (denoted  $r$  as a shorthand) and the  $3M$  nuclear coordinates (denoted  $R$  as a shorthand). In contrast, the electronic Hamiltonian  $H_e$  is a Hermitian differential operator in  $r$ -space but **not** in  $R$ -space. Although  $H_e$  is indeed a function of the  $R$ -variables, it is not a differential operator involving them.

Because  $H_e$  is a Hermitian operator in  $r$ -space, its eigenfunctions  $\Psi_i(r|R)$  obey  $H_e \Psi_i(r|R) = E_i(R) \Psi_i(r|R)$

for any values of the  $R$ -variables, and form a **complete set** of functions of  $r$  for any values of  $R$ . These eigenfunctions and their eigenvalues  $E_i(R)$  depend on  $R$  only because the potentials appearing in  $H_e$  depend on  $R$ . The  $\Psi_i$  and  $E_i$  are the **electronic wavefunctions** and **electronic energies** whose evaluations are treated in the next three Chapters.

The fact that the set of  $\{\Psi_i\}$  is, in principle, complete in  $r$ -space allows the full (electronic and nuclear) wavefunction  $\Psi$  to have its  $r$ -dependence expanded in terms of the  $\Psi_i$  :

$$\Psi(r, R) = \sum_i \Psi_i(r|R) \Xi_i(R).$$

The  $\Xi_i(R)$  functions, carry the remaining  $R$ -dependence of  $\Psi$  and are determined by insisting that  $\Psi$  as expressed here obey the full Schrödinger equation:

$$(H_e + T - E) \sum_i \Psi_i(r|R) \Xi_i(R) = 0.$$

Projecting this equation against  $\langle \Psi_j(r|R) |$  (integrating only over the electronic coordinates because the  $\Psi_j$  are orthonormal only when so integrated) gives:

$$[(E_j(R) - E) \Xi_j(R) + T \Xi_j(R)] = - \sum_i \left[ \langle \Psi_j | T | \Psi_i \rangle (R) \Xi_i(R) + \sum_{a=1,M} \frac{-\hbar^2}{m_a} \langle \Psi_j | \nabla_a | \Psi_i \rangle (R) \cdot \nabla_a \Xi_i(R) \right],$$

where the  $(R)$  notation in  $\langle \Psi_j | T | \Psi_i \rangle (R)$  and  $\langle \Psi_j | \nabla_a | \Psi_i \rangle (R)$  has been used to remind one that the integrals  $\langle \dots \rangle$  are carried out only over the  $r$  coordinates and, as a result, still depend on the  $R$  coordinates.

In the **Born-Oppenheimer** (BO) approximation, one neglects the so-called nonadiabatic or non-BO couplings on the right-hand side of the above equation. Doing so yields the following equations for the  $\Xi_i(R)$  functions:

$$[(E_j(R) - E)\Xi_j^0(R) + T\Xi_j^0(R)] = 0,$$

where the superscript in  $\Xi_j^0(R)$  is used to indicate that these functions are solutions within the BO approximation only.

These BO equations can be recognized as the equations for the **translational, rotational, and vibrational** motion of the nuclei on the 'potential energy surface'  $E_j(R)$ . That is, within the BO picture, the electronic energies  $E_j(R)$ , considered as functions of the nuclear positions  $R$ , provide the potentials on which the nuclei move. The electronic and nuclear-motion aspects of the Schrödinger equation are thereby separated.

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