## Molecular Hamiltonian and the Born–Oppenheimer Approximation

For a molecular system, the Hamiltonian can be written in terms of the kinetic energy of the nuclei (*N*) and electrons (*e*) and the potential energy for the Coulomb interactions of these particles.

$$\begin{aligned}\hat{H} &= \hat{T}_e + \hat{T}_N + \hat{V}_{ee} + \hat{V}_{NN} + \hat{V}_{eN} \\ &= -\sum_{i=1}^{n}\frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{J=1}^{N}\frac{\hbar^2}{2M_J}\nabla_J^2 \\ &\quad + \frac{1}{4\pi\varepsilon_0}\sum_{\substack{i,j=1\\ j>i}}^{n}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|} + \frac{1}{4\pi\varepsilon_0}\sum_{\substack{I,J=1\\ J>I}}^{N}\frac{Z_I Z_J e^2}{|\mathbf{R}_I-\mathbf{R}_J|} - \frac{1}{4\pi\varepsilon_0}\sum_{i=1}^{n}\sum_{J=1}^{N}\frac{Z_J e^2}{|\mathbf{r}_i-\mathbf{R}_J|}\end{aligned} \tag{1}$$

Here and below, we will use lowercase variables to refer to electrons and uppercase to nuclei. The variables *n*, *i*, ***r***, $\nabla_r^2$, and $m_e$ refer to the number, index, position, Laplacian, and mass of electrons, respectively, and *N*, *J*, ***R***, and *M* refer to the nuclei. *e* is the electron charge, and *Z* is the atomic number of the nucleus. Note, this Hamiltonian does not include relativistic effects such as spin-orbit coupling.

We can simplify the expression by defining atomic units for distance and energy. The Bohr radius is defined as

$$a_0 = 4\pi\varepsilon_0\frac{\hbar^2}{m_e e^2} = 5.2918\times 10^{-11} m \tag{2}$$

and the Hartree is

$$E_h = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{a_0} = 4.3598\times 10^{-18} J = 27.2\ eV \tag{3}$$

Written in terms of atomic units, we can see from eq. (3) that the Coulomb potential between an electron and a nucleus becomes $(V/E_h) = -Z/(r/a_0)$, and with eq. (2), the kinetic energy of an electron is $(T/E_h) = a_0^2\nabla^2/2$. Thus the conversion effectively sets the SI variables for $m_e = e = (4\pi\varepsilon_0)^{-1} = \hbar = 1$. Then eq. (1) becomes

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 - \frac{1}{2}\sum_{J=1}^{N}\frac{\nabla_J^2}{M_J} + \sum_{\substack{i,j=1\\ j>i}}^{n}\frac{1}{r_{ij}} + \sum_{\substack{I,J=1\\ J>I}}^{N}\frac{Z_I Z_J}{R_{ij}} - \sum_{i=1}^{n}\sum_{J=1}^{N}\frac{Z_J}{|\mathbf{r}_i-\mathbf{R}_J|} \tag{4}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $R_{ij} = |\mathbf{R}_I - \mathbf{R}_J|$. It is understood that distances and energies are expressed in $a_0$ and $R_h$, and the mass of the nuclei are expressed in units of $m_e = 9.1098\times 10^{-31}$ kg.

The Schrödinger equation is

$$\hat{H}\left(\hat{\mathbf{r}},\hat{\mathbf{R}}\right)\Psi\left(\hat{\mathbf{r}},\hat{\mathbf{R}}\right)=E\Psi\left(\hat{\mathbf{r}},\hat{\mathbf{R}}\right) \quad (5)$$

$\Psi\left(\hat{\mathbf{r}},\hat{\mathbf{R}}\right)$ is the total vibronic wavefunction, where "vibronic" refers to the combined electronic and nuclear eigenstates. Exact solutions using the molecular Hamiltonian are intractable for most problems of interest, so we turn to simplifying approximations. The Born-Oppenheimer approximation is motivated by noting that the nuclei are far more massive than an electron ($m_e \ll M_I$). With this criterion, and when the distances separating particles is not unusually small, the kinetic energy of the nuclei is small relative to the other terms in the Hamiltonian. Physically, this means that the electrons move and adapt rapidly—adiabatically—in response to shifting nuclear positions. This offers an avenue to solving for $\Psi$ by fixing the position of the nuclei, solving for the electronic wavefunctions $\psi_i$, and then iterating for varying R to obtain effective electronic potentials on which the nuclei move.

Since it is fixed for the electronic calculation, we proceed by treating $\boldsymbol{R}$ as a parameter rather than an operator, set $\hat{T}_N$ to 0, and solve the electronic TISE:

$$\hat{H}_{el}\left(\hat{\mathbf{r}},\mathbf{R}\right)\psi_i\left(\hat{\mathbf{r}},\mathbf{R}\right)=U_i\left(\mathbf{R}\right)\psi_i\left(\hat{\mathbf{r}},\mathbf{R}\right) \quad (6)$$

$U_i$ are the electronic energy eigenvalues for the fixed nuclei, and the electronic Hamiltonian in the BO approximation is

$$\hat{H}_{el}=\hat{T}_e+\hat{V}_{ee}+\hat{V}_{eN} \quad (7)$$

In (6), $\psi_i$ is the electronic wavefunction for fixed $\boldsymbol{R}$, with $i$ = 0 referring to the electronic ground state. Repeating this calculation for varying $\boldsymbol{R}$, we obtain $U_i(\boldsymbol{R})$, an effective or mean-field potential for the electronic states on which the nuclei can move. These effective potentials are known as Born–Oppenheimer or adiabatic potential energy surfaces (PES).

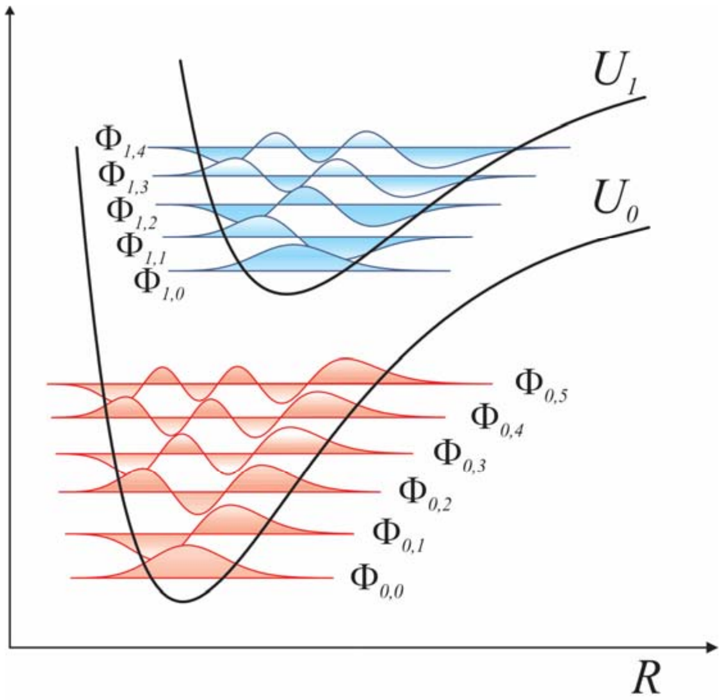
For the nuclear degrees of freedom, we can define a Hamiltonian for the $i^{\text{th}}$ electronic PES:

$$\hat{H}_{Nuc,i}=\hat{T}_N+U_i(\hat{R}) \quad (8)$$

which satisfies a TISE for the nuclear wave functions $\Phi(R)$:

$$\hat{H}_{Nuc,i}\Phi_{iJ}(R)=E_{iJ}\Phi_{iJ}(R) \quad (9)$$

Here $J$ refers to the $J^{\text{th}}$ eigenstate for nuclei evolving on the $i^{\text{th}}$ PES. Equation (8) is referred to as the Born-Oppenheimer Hamiltonian.




The BOA effectively separates the nuclear and electronic contributions to the wavefunction, allowing us to express the total wavefunction as a product of these contributions $\Psi(\mathbf{r},\mathbf{R}) = \Phi(\mathbf{R})\psi(\mathbf{r},\mathbf{R})$ and the eigenvalues as sums over the electronic and nuclear contribution: $E = E_N + E_e$.