

The molecular Schrödinger equation

Remark 1. The non-relativistic Hamiltonian of a system of nuclei and electrons includes a kinetic energy operator for each particle and a Coulomb operator for each particle pair.¹

$$\hat{H}(\mathbf{r}_e, \mathbf{r}_n) = \hat{T}^e + \hat{T}^n + V^e(\mathbf{r}_e) + V^n(\mathbf{r}_n) + V^{e,n}(\mathbf{r}_e, \mathbf{r}_n) \quad \hat{T}^x = \frac{1}{2m_x} \sum \hat{\mathbf{p}}_{x,i}^2 \quad V^{x,y}(\mathbf{r}_x, \mathbf{r}_y) = \frac{1}{4\pi\epsilon_0} \sum \frac{q_x q_y}{\|\mathbf{r}_{x,i} - \mathbf{r}_{y,j}\|^2} \quad (1)$$

The state of this system is described by a wavefunction, $\Psi_\alpha^{\text{tot}}(\mathbf{r}_e, \mathbf{r}_n, t)$, which is governed by the Schrödinger equation.

$$\hat{H}(\mathbf{r}_e, \mathbf{r}_n) \Psi_\alpha^{\text{tot}}(\mathbf{r}_e, \mathbf{r}_n, t) = i\hbar \frac{\partial \Psi_\alpha^{\text{tot}}(\mathbf{r}_e, \mathbf{r}_n, t)}{\partial t} \quad (2)$$

In the absence of external fields the system exists in a *stationary state*. Stationary states are characterized by a static wavefunction $\Psi_\alpha^{\text{tot}}(\mathbf{r}_e, \mathbf{r}_n)$ with a conserved energy expectation value E_α^{tot} that controls its frequency of oscillation in time. These quantities are governed by a Hamiltonian eigenvalue equation, which is the *time-independent Schrödinger equation*.

$$\hat{H}(\mathbf{r}_e, \mathbf{r}_n) \Psi_\alpha^{\text{tot}}(\mathbf{r}_e, \mathbf{r}_n) = E_\alpha^{\text{tot}} \Psi_\alpha^{\text{tot}}(\mathbf{r}_e, \mathbf{r}_n) \quad \Psi_\alpha^{\text{tot}}(\mathbf{r}_e, \mathbf{r}_n, t) = \Psi_\alpha^{\text{tot}}(\mathbf{r}_e, \mathbf{r}_n) e^{-\frac{i}{\hbar} E_\alpha^{\text{tot}} t} \quad (3)$$

If $\mathcal{H}^e \equiv \{\Phi_k(\mathbf{r}_e) | k\}$ is a complete basis of functions in \mathbf{r}_e , the time-independent wavefunction can be expanded as follows.²³

$$\Psi_\alpha^{\text{tot}}(\mathbf{r}_e, \mathbf{r}_n) = \sum_{k'} \Phi_{k'}(\mathbf{r}_e) \chi_{k',\alpha}(\mathbf{r}_n) \quad (4)$$

Substituting this into equation 3 and integrating with $\Phi_k^*(\mathbf{r}_e)$ yields an equation for the unknown nuclear functions.

$$\hat{H}(\mathbf{r}_n) \chi_\alpha(\mathbf{r}_n) = E_\alpha^{\text{tot}} \chi_\alpha(\mathbf{r}_n) \quad \hat{H}_{k,k'}(\mathbf{r}_n) \equiv \int d^{n_e} \mathbf{r}_e \Phi_k^*(\mathbf{r}_e) \hat{H}(\mathbf{r}_e, \mathbf{r}_n) \Phi_{k'}(\mathbf{r}_e) \quad \chi_\alpha(\mathbf{r}_n) = \begin{pmatrix} \chi_{0,\alpha}(\mathbf{r}_n) \\ \chi_{1,\alpha}(\mathbf{r}_n) \\ \vdots \end{pmatrix} \quad (5)$$

This operator matrix equation can be solved by further expanding each entry in a basis for nuclear function space, yielding a supermatrix eigenvalue equation with scalar coefficients. Exact solution of this equation is computationally intractable because the electronic and nuclear function spaces are infinite-dimensional. In practice this can be resolved by “coarse-graining” each space with a finite subset of carefully chosen functions.

Definition 1. The Born-Oppenheimer approximation. The *Born-Oppenheimer approximation* decouples the electrons from the nuclei by neglecting the nuclear kinetic energy operator, $\hat{H}^{\text{bo}}(\mathbf{r}_e, \mathbf{r}_n) \equiv \hat{H}(\mathbf{r}_e, \mathbf{r}_n) - \hat{T}^n$, and treating nuclear attraction as a fixed external potential. The resulting *electronic Schrödinger equation* has the form

$$\hat{H}^{\text{bo}}(\mathbf{r}_e, \mathbf{r}_n) \Psi_k^e(\mathbf{r}_e, \mathbf{r}_n) = E_k^e(\mathbf{r}_n) \Psi_k^e(\mathbf{r}_e, \mathbf{r}_n) \quad (6)$$

which is a continuous series of eigenvalue equations parametrized by \mathbf{r}_n . The index k refers to the *electronic state* of the molecule, which is a construct of the Born-Oppenheimer approximation. The *noncrossing rule* says that these electronic energies form non-intersecting *potential energy surfaces* over the space of nuclear coordinates, $\{E_k^e(\mathbf{r}_n) | \mathbf{r}_n\}$.⁴ To construct a total molecular wavefunction, the Born-Oppenheimer approximation employs two simplifying assumptions.

$$\Psi_\alpha^{\text{tot}} \approx \Psi_{k\nu}^{\text{bo}} \quad \text{where} \quad \Psi_{k\nu}^{\text{bo}}(\mathbf{r}_e, \mathbf{r}_n) \equiv \Psi_k^e(\mathbf{r}_e, \mathbf{r}_n) \chi_{k,\nu}^{\text{bo}}(\mathbf{r}_n) \quad [\hat{T}^n, \Psi_k^e(\mathbf{r}_e, \mathbf{r}_n)] \approx 0 \quad (7)$$

Applying these to the exact Schrödinger equation yields a *rovibrational Schrödinger equation* for the nuclear component.

$$(\hat{T}^n + E_k^e(\mathbf{r}_n)) \chi_{k,\nu}^{\text{bo}}(\mathbf{r}_n) = E_{k,\nu}^{\text{bo}} \chi_{k,\nu}^{\text{bo}}(\mathbf{r}_n) \quad (8)$$

This scheme results in a good approximation to the wavefunction under the following two conditions: 1. The nuclear wavefunction $\chi_{k,\nu}^{\text{bo}}(\mathbf{r}_n)$ is localized to a region where the potential energy surface $E_k^e(\mathbf{r}_n)$ is well-separated from its neighboring surfaces; and 2. The electronic wavefunction $\Psi_k^e(\mathbf{r}_e, \mathbf{r}_n)$ is slowly varying in \mathbf{r}_n over that region.

Remark 2. The electronic Schrödinger equation can also be used as a stepping stone to the exact molecular wavefunction, circumventing the approximations of equation 7. Namely, equation 6 can be used to generate a convenient electronic basis for equations 4 and 5. The dependence of the electronic states on \mathbf{r}_n admits two sensible choices for \mathcal{H}^e .

$$\text{I} \mathcal{H}^e \equiv \{\Psi_k^e(\mathbf{r}_e, \mathbf{r}_n^\circ) | k\} \quad \text{II} \mathcal{H}^e \equiv \{\Psi_k^e(\mathbf{r}_e, \mathbf{r}_n) | k\} \quad (9)$$

Option I is the *Longuet-Higgins representation*, which uses Born-Oppenheimer electronic states from a fixed point on the potential surface. Option II is the *Born representation*, which associates each set of nuclear coordinates with its own set of electronic functions. Both options approach the exact non-relativistic wavefunction in the limit of an infinite expansion, but the Born representation is more amenable to coarse-graining with a small number of functions. The Longuet-Higgins representation is appropriate when the probability density of the nuclei is localized within a narrow region around \mathbf{r}_n° , as might be observed at a deep well on the potential surface.

¹For $x = y$ one must restrict the sum on the right to unique i, j pairs in order to avoid double-counting.

³By resolution of the identity, the nuclear functions can be identified as $\chi_{k,\alpha}(\mathbf{r}_n) = \int d^{n_e} \mathbf{r}_e \Phi_k^*(\mathbf{r}_e) \Psi_\alpha^{\text{tot}}(\mathbf{r}_e, \mathbf{r}_n)$.

⁴More precisely, electronic states of a given spin and spatial symmetry do not intersect.

Remark 3. To contrast the two alternatives in rmk 2, express the Hamiltonian as $\hat{H}(\mathbf{r}_e, \mathbf{r}_n) = \hat{T}^n + \hat{H}^{\text{bo}}(\mathbf{r}_e, \mathbf{r}_n)$ and consider its matrix elements for each set of electronic functions.

$$\hat{\mathbf{H}}(\mathbf{r}_n) = \hat{\mathbf{T}}^n + \mathbf{H}^{\text{bo}}(\mathbf{r}_n) \quad H_{k,k'}^{\text{bo}}(\mathbf{r}_n) \equiv \int d^n \mathbf{r}_e \Phi_k^*(\mathbf{r}_e) \hat{H}^{\text{bo}}(\mathbf{r}_e, \mathbf{r}_n) \Phi_{k'}(\mathbf{r}_e) \quad \hat{T}_{k,k'}^n(\mathbf{r}_n) \equiv \int d^n \mathbf{r}_e \Phi_k^*(\mathbf{r}_e) \hat{T}^n \Phi_{k'}(\mathbf{r}_e) \quad (10)$$

Assuming the electronic basis states are orthonormal,⁵ the matrix elements of \hat{T}^n can be written as follows.⁶

$$\hat{T}_{k,k'}^n = \delta_{kk'} \hat{T}^n + \hat{\Lambda}_{k,k'}^n \quad \hat{\Lambda}_{k,k'}^n \equiv \int d^n \mathbf{r}_e \Phi_k^*(\mathbf{r}_e) [\hat{T}^n, \Phi_{k'}(\mathbf{r}_e)] \quad (11)$$

$$H_{k,k'}^{\text{bo}}(\mathbf{r}_n) = \delta_{kk'} E_k^e(\mathbf{r}_n) + \bar{H}_{k,k'}^{\text{bo}}(\mathbf{r}_n) \quad \bar{H}_{k,k'}^{\text{bo}}(\mathbf{r}_n) \equiv \int d^n \mathbf{r}_e \Phi_k^*(\mathbf{r}_e) (\hat{H}^{\text{bo}}(\mathbf{r}_e, \mathbf{r}_n) - E_k^e(\mathbf{r}_n)) \Phi_{k'}(\mathbf{r}_e) \quad (12)$$

The structure of these matrices is characterized by the following relationships

$$[\hat{T}^n, \Psi_k^e(\mathbf{r}_e, \mathbf{r}_n^\circ)] = 0 \quad (\hat{H}^{\text{bo}}(\mathbf{r}_e, \mathbf{r}_n) - E_k^e(\mathbf{r}_n)) \Psi_k(\mathbf{r}_e, \mathbf{r}_n^\circ) \neq 0 \quad (13)$$

$$[\hat{T}^n, \Psi_k^e(\mathbf{r}_e, \mathbf{r}_n)] \neq 0 \quad (\hat{H}^{\text{bo}}(\mathbf{r}_e, \mathbf{r}_n) - E_k^e(\mathbf{r}_n)) \Psi_k(\mathbf{r}_e, \mathbf{r}_n) = 0 \quad (14)$$

which follow from equation 6 and the fact that \hat{T}^n is a differential operator in \mathbf{r}_n . In words, this says that the Longuet-Higgins representation diagonalizes the nuclear kinetic energy operator, whereas the Born representation diagonalizes the Born-Oppenheimer potential.

Remark 4. In the Longuet-Higgins representation, the nuclear motion problem is typically solved by expanding the Hamiltonian in a Taylor series at \mathbf{r}_n° , which can be expressed as follows.

$${}^I \hat{\mathbf{H}}(\mathbf{r}_n) = \hat{T}^n \mathbf{1} + \mathbf{E}^e(\mathbf{r}_n) + \frac{\partial \mathbf{H}^{\text{bo}}(\mathbf{r}_n^\circ)}{\partial \mathbf{r}_n} \cdot \delta \mathbf{r}_n + \frac{1}{2} \delta \mathbf{r}_n \cdot \frac{\partial^2 \mathbf{H}^{\text{bo}}(\mathbf{r}_n^\circ)}{\partial \mathbf{r}_n \partial \mathbf{r}_n} \cdot \delta \mathbf{r}_n + \dots \quad \mathbf{E}^e(\mathbf{r}_n) \equiv \begin{pmatrix} E_0^e(\mathbf{r}_n) & 0 & \dots \\ 0 & E_1^e(\mathbf{r}_n) & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \quad (15)$$

This approach leads to the Köppel-Domcke-Cederbaum (KDC) approximation to the total molecular wavefunction.

Remark 5. The Born-representation Hamiltonian has the following structure.

$${}^{\text{II}} \hat{\mathbf{H}}(\mathbf{r}_n) = \hat{T}^n \mathbf{1} + \hat{\Lambda}^n(\mathbf{r}_n) + \mathbf{E}^e(\mathbf{r}_n) \quad \hat{\Lambda}_{k,k'}^n(\mathbf{r}_n) = \int d^n \mathbf{r}_e \Psi_k^{e*}(\mathbf{r}_e, \mathbf{r}_n) [\hat{T}^n, \Psi_{k'}^e(\mathbf{r}_e, \mathbf{r}_n)] \quad (16)$$

Although this approach leads to a more compact wavefunction expansion, it is considerably more complicated to work with because the elements of the coupling matrix $\hat{\Lambda}^n$ involve derivatives of the electronic states with respect to \mathbf{r}_n .

Definition 2. The adiabatic approximation. Neglecting the off-diagonal elements of the coupling matrix in the Born representation leads to the *adiabatic approximation*, which is equivalent to employing the Born-Oppenheimer separability assumption, $\Psi_{k,\nu}^{\text{ad}}(\mathbf{r}_e, \mathbf{r}_n) = \Psi_k^e(\mathbf{r}_e, \mathbf{r}_n) \chi_{k,\nu}^{\text{ad}}(\mathbf{r}_n)$, without the vanishing commutator approximation. The nuclear functions in the adiabatic approximation satisfy a set of conditions similar to equation 8.

$$(\hat{T}^n + \hat{\Lambda}_{k,k}^n(\mathbf{r}_n) + E_k^e(\mathbf{r}_n)) \chi_{k,\nu}^{\text{ad}}(\mathbf{r}_n) = E_{k,\nu}^{\text{ad}} \chi_{k,\nu}^{\text{ad}}(\mathbf{r}_n) \quad (17)$$

Definition 3. The diagonal Born-Oppenheimer approximation. First-order perturbation theory leads to an even simpler alternative to the adiabatic approximation, known as the *diagonal Born-Oppenheimer correction*.

$$E_{k,\nu}^{\text{ad}} \approx E_{k,\nu}^{\text{bo}} + \Delta_k^{\text{dboc}}(\mathbf{r}_n) \quad \Delta_k^{\text{dboc}}(\mathbf{r}_n) = \int d^n \mathbf{r}_e \Psi_k^{e*}(\mathbf{r}_e, \mathbf{r}_n) \hat{T}^n \Psi_k^e(\mathbf{r}_e, \mathbf{r}_n) \quad (18)$$

⁵As a Hermitian operator, the Born-Oppenheimer model Hamiltonian always possesses an orthonormal set of eigenstates.

⁶Using $\hat{T}^n \Phi_k(\mathbf{r}_n) = \Phi_k(\mathbf{r}_n) \hat{T}^n + [\hat{T}^n, \Phi_k(\mathbf{r}_n)]$.