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]

$$\hat{H}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}) = \hat{T}^\text{e} + \hat{T}^\text{n} + V^\text{e}(\mathbf{r}_\text{e}) + V^\text{n}(\mathbf{r}_\text{n}) + V^\text{e,n}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}) \quad \hat{T}^\text{x} = \frac{1}{2m_\text{x}} \sum \hat{\mathbf{p}}_{\text{x},i}^2 \quad V^\text{x,y}(\mathbf{r}_\text{x}, \mathbf{r}_\text{y}) = \frac{1}{4\pi\varepsilon_0} \sum \frac{q_\text{x} q_\text{y}}{\|\mathbf{r}_{\text{x},i} - \mathbf{r}_{\text{y},j}\|^2} \quad (1)$$

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

$$\hat{H}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}) \Psi_\alpha^\text{tot}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}, t) = i\hbar \frac{\partial \Psi_\alpha^\text{tot}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}, t)}{\partial t} \tag{2}$$

In the absence of external fields the system exists in a *stationary state*. Stationary states are characterized by a static wavefunction $\Psi_\alpha^\text{tot}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n})$ and 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*.

$$\hat{H}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}) \Psi_\alpha^\text{tot}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}) = E_\alpha^\text{tot} \Psi_\alpha^\text{tot}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}) \qquad \Psi_\alpha^\text{tot}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}, t) = \Psi_\alpha^\text{tot}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}) e^{-\frac{i}{\hbar} E_\alpha^\text{tot} t} \tag{3}$$

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

$$\Psi_\alpha^\text{tot}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}) = \sum_{k'} \Phi_{k'}(\mathbf{r}_\text{e}) \, \chi_{k',\alpha}(\mathbf{r}_\text{n}) \tag{4}$$

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

$$\hat{\mathbf{H}}(\mathbf{r}_\text{n}) \boldsymbol{\chi}_\alpha(\mathbf{r}_\text{n}) = E_\alpha^\text{tot} \boldsymbol{\chi}_\alpha(\mathbf{r}_\text{n}) \qquad \hat{H}_{k,k'}(\mathbf{r}_\text{n}) \equiv \int d^{n_\text{e}}\mathbf{r}_\text{e} \, \Phi_k^*(\mathbf{r}_\text{e}) \hat{H}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}) \Phi_{k'}(\mathbf{r}_\text{e}) \qquad \boldsymbol{\chi}_\alpha(\mathbf{r}_\text{n}) = \begin{pmatrix} \chi_{0,\alpha}(\mathbf{r}_\text{n}) \\ \chi_{1,\alpha}(\mathbf{r}_\text{n}) \\ \vdots \end{pmatrix} \tag{5}$$

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, $\hat{H}^\text{bo}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}) \equiv \hat{H}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}) - \hat{T}^\text{n}$, and treating nuclear attraction as a fixed external potential. The resulting *electronic Schrödinger equation* has the form

$$\hat{H}^\text{bo}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}) \Psi_k^\text{e}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}) = E_k^\text{e}(\mathbf{r}_\text{n}) \Psi_k^\text{e}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}) \tag{6}$$

which is a continuous series of eigenvalue equations parametrized by $\mathbf{r}_\text{n}$. 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, $\{E_k^\text{e}(\mathbf{r}_\text{n}) \,|\, \mathbf{r}_\text{n}\}$.[2] To construct a total molecular wavefunction, the Born-Oppenheimer approximation employs two simplifying assumptions.

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

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

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

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

$$^\text{I}\mathcal{H}^\text{e} \equiv \{\Psi_k^\text{e}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}^\circ) \,|\, k\} \qquad\qquad ^\text{II}\mathcal{H}^\text{e} \equiv \{\Psi_k^\text{e}(\mathbf{r}_\text{e}, \mathbf{r}_\text{n}) \,|\, k\} \tag{9}$$

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 $\mathbf{r}_\text{n}^\circ$, as might be observed at a deep well on the potential surface.

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

[2] More 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 $\hat{H}(\mathbf{r}_e, \mathbf{r}_n) = \hat{T}^n + \hat{H}^{bo}(\mathbf{r}_e, \mathbf{r}_n)$ and consider its matrix elements for each set of electronic functions.

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

Assuming the electronic basis states are orthonormal,[3] the matrix elements of $\hat{T}^n$ can be written as follows.[4]

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

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

The structure of these matrices is characterized by the following relationships

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

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

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 $\mathbf{r}_n^\circ$, which can be expressed as follows.

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

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.

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

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 $\hat{\mathbf{\Lambda}}^n$ 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, $\Psi_{k,\nu}^{ad}(\mathbf{r}_e, \mathbf{r}_n) = \Psi_k^e(\mathbf{r}_e, \mathbf{r}_n)\chi_{k,\nu}^{ad}(\mathbf{r}_n)$, without the vanishing commutator approximation. The nuclear functions in the adiabatic approximation satisfy a set of conditions similar to equation 8.

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

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*.

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

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

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