The Quantum Mechanical Base

The Molecular Schrödinger Equation

The Schrödinger equation is the quantum mechanical description for a system in the quantum reality. It is the equivalent to Newton's mechanical interpretation for a quantum mechanical system and in its most general form it is given by

$$i\hbar\frac{\partial}{\partial t}\Psi(t,\mathbf{x}) = \hat{H}\Psi(t,\mathbf{x}) \tag{1}$$

In this equation, $\hat{H}$ is the Hamiltonian operator, which contains a description of all the interactions in the system. This is then the energy operator in quantum mechanics. $\mathbf{x}$ is the vectorial description of the position for all particles in an N-dimensional space. If the Hamiltonian is time independent, then time and spatial coordinates become separable.

$$i\hbar\frac{\partial}{\partial t}\Psi(t,\mathbf{x}) = i\hbar\frac{\partial}{\partial t}\upsilon(t)\psi(\mathbf{x}) = \hat{H}\upsilon(t)\psi(\mathbf{x})$$

From this separation of variables we obtain two hopefully simpler differential equations to solve. One equations gives the time evolution,

$$i\hbar\frac{\partial}{\partial t}\upsilon(t) = E\upsilon(t)$$

and the other the position description of the quantum mechanical system.

$$\hat{H}\psi(\mathbf{x}) = E\psi(\mathbf{x})$$

Both these equations are eigenvalue-equations. Since molecular Hamiltonians are typically time independent, we need only to concern ourselves with solving the time-independent Schrödinger equation.

For a single molecule we include all electron-electron interactions, as well as all interactions between the many nuclei and between the nuclei and electrons. Since we have a system with many nuclei and electrons, we do not have a unique referential for the coordinate system. In a very general form, this Schrödinger equation is given by

$$\left(\hat{T}_e + \hat{T}_n + \hat{V}_{ee} + \hat{V}_{ne} + \hat{V}_{nn}\right)\Psi = \hat{H}\Psi = E\Psi \tag{2}$$

where the operator $\hat{T}_i$ gives the kinetic energy term for the particle type i and the $\hat{V}_{ij}$ terms the interaction between particle types i and j. As indices, the letters e and n refer to electrons and nuclei respectively. The kinetic energy and potential operators have in general the form

$$\hat{T}_i = -\sum\nolimits_{a\in i} \frac{\hbar^2}{2m_a}\nabla^2_{\mathbf{r}_a} \tag{3}$$

$$\hat{V}_{ii} = \frac{1}{2}\sum_{a,b\in i}\sum_{b\neq a}\frac{Z_a Z_b e^2}{4\pi\epsilon_0|\mathbf{r}_a - \mathbf{r}_b|} \tag{4}$$

$$\hat{V}_{en} = -\sum_{a\in e}\sum_{b\in n}\frac{Z_b e^2}{4\pi\epsilon_0|\mathbf{r}_a - \mathbf{R}_b|} \tag{5}$$

In the summations, e refers to the elementary charge, Z_i the charge number of particle i, ϵ_0 the dielectric constant of the vacuum, and $\mathbf{r}_i$ the coordinates of particle i (in the case of nuclei, whenever possible, we used capital letters). With this approximation we assume that all particles in the system are point-wise and relativity effects are also neglected (*1*). Note that the Hamiltonian above disregards N-body terms, which means that it considers only pairwise-interactions.

Just like the polyelectronic Schrödinger equation for atoms (one nucleus, many electrons), the molecular Schrödinger equation has no analytic solutions and special techniques must be used to obtain an approximate solution.

The Born-Oppenheimer Approximation

The molecular Schrödinger equation is a function of the electronic and nuclear coordinates. As one can see from the definition of the $\hat{V}_{en}$ potential, one cannot separate the nuclear coordinates from the electronic coordinates. The most general solution to the molecular Schrödinger equation is then a function of the form $\Psi\left(\mathbf{R},\mathbf{r}\right)$ where $\mathbf{R}$ are the nuclear coordinates and $\mathbf{r}$ the electronic coordinates. However, in most cases, like in stable structures, this dependence is parametric, a consequence of the different time-frames in which nuclei and electrons move. This can be easily seen by the fact that nuclei are at least approximately 1000 times heavier than electrons. As a consequence, their motion is slower and the total molecular wavefunction can be partitioned in the form $\Psi\left(\mathbf{R},\mathbf{r}\right) = \psi^{nuc}\left(\mathbf{R}\right)\times\psi^{el}\left(\mathbf{r}|\bar{\mathbf{R}}\right)$, where "$|\bar{\mathbf{R}}$" indicates the parametric dependence: the electronic wavefunction is a function of the nuclear coordinates and the electrons will then act as a potential on which the nuclei move. Applying this definition of the wavefunction in the Schrödinger equation

$$\left(\hat{T}_e + \hat{T}_n + \hat{V}_{ee} + \hat{V}_{ne} + \hat{V}_{nn}\right)\psi^{nuc}\left(\mathbf{R}\right)\times\psi^{el}\left(\mathbf{r}|\bar{\mathbf{R}}\right) = E\psi^{nuc}\left(\mathbf{R}\right)\times\psi^{el}\left(\mathbf{r}|\bar{\mathbf{R}}\right)$$

$$\begin{aligned}\left(\hat{T}_e+\hat{V}_{ee}+\hat{V}_{ne}\right)\psi^{nuc}\left(\mathbf{R}\right)\times\psi^{el}\left(\mathbf{r}|\bar{\mathbf{R}}\right)+\left(\hat{T}_n+\hat{V}_{nn}\right)\psi^{nuc}\left(\mathbf{R}\right)\times\psi^{el}\left(\mathbf{r}|\bar{\mathbf{R}}\right)\\=E\psi^{nuc}\left(\mathbf{R}\right)\times\psi^{el}\left(\mathbf{r}|\bar{\mathbf{R}}\right)\end{aligned}\tag{6}$$

As a first approximation, we consider that the nuclei are fixed. Thus, the $\hat{T}_n$ term is zero. None of the remaining operators contain derivatives with respect to nuclear coordinates. This means that operator and wavefunction commute and multiplication to the left by the complex conjugate of the nuclear wavefunction leads to the electronic Schrödinger equation

$$\left(\hat{T}_e+\hat{V}_{ee}+\hat{V}_{ne}\right)\psi^{el}\left(\mathbf{r}|\bar{\mathbf{R}}\right)+E_{nuc}\psi^{el}\left(\mathbf{r}|\bar{\mathbf{R}}\right)=E\psi^{el}\left(\mathbf{r}|\bar{\mathbf{R}}\right)$$

which can be rearranged to

$$\hat{H}^{el}\psi^{el}\left(\mathbf{r}|\bar{\mathbf{R}}\right)=\left(E-E_{nuc}\right)\psi^{el}\left(\mathbf{r}|\bar{\mathbf{R}}\right)=E_{el}\psi^{el}\left(\mathbf{r}|\bar{\mathbf{R}}\right)\tag{7}$$

Note that just like the electronic wavefunction, the electronic energy is a function of the nuclear coordinates. Multiplication of 1.6 by the complex conjugate of the electronic wavefunction gives

$$E_{el}(\mathbf{R})\psi^{nuc}\left(\mathbf{R}\right)+\hat{T}_n\psi^{nuc}\left(\mathbf{R}\right)=E\psi^{nuc}\left(\mathbf{R}\right)$$

which is rearranged to

$$\left(\hat{T}_n+E_{el}(\mathbf{R})\right)\psi^{nuc}\left(\mathbf{R}\right)=E\psi^{nuc}\left(\mathbf{R}\right)\tag{8}$$

Solving equation 1.7 gives the electronic structure of molecules. The solutions of 1.8 describe the nuclear motion and states, namely molecular vibration, rotation and even translation.

Translations, Rotations and Vibrations

In the previous section, the motion of electrons was separated from the motion of nuclei in the Schrödinger equation. We will now work on the nuclear wavefunction to simplify it further. The potential surface created by electrons on which nuclei move cannot be obtained analytically. It is possible to calculate a specific point of this surface with any accuracy desired. However, a closed analytical form is not known. This potential describes how much energy is required to give to the system in order to move the nuclei in a given direction (*2*).

By changing the nuclear Schrödinger equation into the set of coordinates for the position of the center of mass and all other internal coordinates, then we can split equation

1.8 into two further problems: one deals with molecular translation and is tridimensional; the other deals with internal motion and has dimension $3N-3$, where N is the total number of atoms.

For an isolated molecule (or a whole system of these), the translational equation corresponds simply to a free-particle (inside a box of volume V?). The Schrödinger equation for internal motion is however not straightforward to solve, especially due to the dependence on the electronic potential. To get an approximate solution we apply two further approximations. The first one is that the radial and angular parts of the internal motion are independent of one another. This yields the separation of the internal motion into rotations and vibrations. Because of this separation, rotations are stiff (the molecule has a rigid structure that corresponds to a minimum in the electronic potential surface) and the main model employed is the rigid rotor. This means that upon increased rotational velocity, molecules are not allowed to be deformed in the model. The second approximation allows one to approximately solve the vibrational Schrödinger equation and it consists in the harmonic oscillator approximation. These models are further developed in other documents.

From this construction we may therefore conclude that completely solving the molecular Schrödinger equation requires solving four different Schrödinger equations, as the Hamiltonian is separable in four main contributions:

$$\hat{H}\psi(\mathbf{x},\mathbf{X}) = \left(\hat{H}_{trans} + \hat{H}_{rot} + \hat{H}_{vib} + \hat{H}_{elec}\right)\psi(\mathbf{x},\mathbf{X})$$

$$= \left(\hat{H}_{trans} + \hat{H}_{rot} + \hat{H}_{vib} + \hat{H}_{elec}\right)\psi^{trans}(\mathbf{X})\psi^{rot}(\mathbf{X})\psi^{vib}(\mathbf{X})\psi^{elec}(\mathbf{x}|\mathbf{X})$$

$$= \left(E_{trans} + E_{rot} + E_{vib} + E_{elec}\right)\psi^{trans}(\mathbf{X})\psi^{rot}(\mathbf{X})\psi^{vib}(\mathbf{X})\psi^{elec}(\mathbf{x}|\mathbf{X}) = E\psi(\mathbf{x},\mathbf{X})$$

The complete wavefunction is thus the product of four subcomponents and the energy is the sum of four "independent" contributions (independence only within the set of approximations used).

Energy Separability

Whenever the different contributions to energy are weakly coupled (as in the discussion above), the system's energy can be separated into translations, rotations, vibrations and electronic energy. This weak coupling is however not always a valid approximation. Separating the rovibrations from the electronic energy is valid only under the Born-Oppenheimer approximation (*3*). Whenever a system violates the separation of nuclear internal motion from the electronic motion this separation does not take place. Typical cases in which the Born-Oppenheimer approximation is violated are conical intersections. Conical intersections are a set of nuclear arrangements for which different electronic states intersect. These are not such uncommon findings in computational chemistry studies. For instance, the cis-trans isomerisation of ethylenes (*e.g.*, $2-butene$) is dominated and controlled by a conical intersection.

Furthermore, the separation of the rotational motion from vibrations is possible under the rigid rotor approximation (*3*). If the molecules are large enough to feel centrifugal forces, the inertia matrix is not the same for all excited rotational states and the rigid rotor model breaks down.

Bibliography

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