

Molecular structure: Separating electronic and nuclear motion

Notes on Quantum Mechanics

<http://quantum.bu.edu/notes/QuantumMechanics/MolecularStructure.pdf>
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While electrons are very much lighter than nuclei, both experience comparable (Coulombic) potential energies.

- | Calculate the potential energy, in eV, of two protons separated by 1 Å.
- | Calculate the potential energy, in eV, of an electron and a proton separated by 1 Å.

The result is that electrons move much faster than nuclei. This in turn means that the characteristic frequencies of electronic motion are much higher than those of nuclear (vibrational and rotational) motion, and so electronic spectroscopic transitions occur in more energetic regions of the spectrum (visible, UV, and X-ray) than do vibrational (IR) and rotational (microwave) spectroscopic transitions.

The way to develop this idea quantitatively is to use the large mass difference between electrons and nuclei to try to treat their motion separately. It turns out that this can be done using two key ideas, known as the *adiabatic approximation* and the *Born-Oppenheimer approximation*. The result is separate Schrödinger equations for the electronic and the nuclear motion.

■ Adiabatic approximation

The mathematical implementation of the separation of electronic and nuclear motion proceeds in two steps. The first step is known as the *adiabatic approximation*.

We start with the full molecular hamiltonian, which we can write schematically as

$$H = -\frac{\hbar^2}{2} \sum_n \frac{1}{M_n} \nabla_n^2 - \frac{\hbar^2}{2m} \sum_e \nabla_e^2 + V(R, r).$$

In this expression n labels the nuclei and e labels the electrons; r and R denote the collection of electronic and nuclear coordinates, respectively; the operators ∇^2 are the sums of second derivatives of the corresponding coordinates; and $V(R, r)$ is the potential energy function for the attraction of each electron to each nucleus, the repulsion of each electron by all of the other electrons, and the repulsion of each nucleus by all of the other nuclei.

- | Write down the expression for H for hydrogen molecule. Label the nuclei a and b and label the electrons 1 and 2.

In the limit that the nuclei in a molecule are far heavier than the electrons, that is, when $m/M_n \approx 0$, the nuclear kinetic energy is negligible compared to the electronic kinetic energy and the potential energy,

$$\lim_{m/M_n \rightarrow 0} H = H_\infty = -\frac{\hbar^2}{2m} \sum_e \nabla_e^2 + V(R, r).$$

This *infinite nuclear mass hamiltonian*, H_∞ , describes electronic motion with respect to a *fixed nuclear framework*. Such a description of electronic motion will be the more exact the closer the value of m/M_n is to zero.

For each possible set of nuclear positions, R , we can solve the infinite mass Schrödinger equation,

$$H_\infty \psi_i(R, r) = E_i(R) \psi_i(R, r).$$

In this equation the eigenfunctions $\psi_i(R, r)$ and eigenvalues $E_i(R)$ of H_∞ will depend on the nuclear coordinates R *parametrically*. The reason is that the potential energy $V(R, r)$ is different for different sets R of nuclear positions. This parametric dependence amounts to saying that the nuclei remain at fixed positions R and that the electronic motion takes place in the potential $V(R, r)$ corresponding to this fixed nuclear framework. For a given R we obtain the set of eigenvalues $E_1(R), E_2(R), \dots$, where the subscripts 1, 2, \dots , denotes the set of electronic quantum numbers. For a particular eigenvalue, say $E_k(R)$, we can vary the nuclear framework and thereby obtain a *potential energy surface* E_k on which the nuclear motion takes place.

To see this, we express a solution $\Psi_\mathcal{E}(R, r)$ to the full molecular Schrödinger equation

$$H \Psi_\mathcal{E}(R, r) = \mathcal{E} \Psi_\mathcal{E}(R, r),$$

with total energy \mathcal{E} , in terms of the electronic eigenfunctions as

$$\Psi_\mathcal{E}(R, r) = \sum_i \psi_i(R, r) \phi_i(R).$$

It is crucial to appreciate that in this expansion the *expansion coefficients are functions of the nuclear coordinates*,

$$\phi_i(R) = \int \psi_i(R, r)^* \Psi_\mathcal{E}(R, r) dr.$$

The reason this is so is that the electronic eigenfunctions form a complete set,

$$\delta(r - r') = \sum_j \psi_j(R, r) \psi_j^*(R, r').$$

for *each nuclear geometry* R .

Because of the completeness of the electronic eigenfunctions $\psi_i(R, r)$ for each nuclear geometry and dependence of the expansion coefficients $\phi_i(R)$ on nuclear geometry, the expansion of the full molecular wave function $\Psi_\mathcal{E}(R, r)$ is exact. We can generate a linear system for the expansion coefficients $\phi_i(R)$ using the method we have learned. The result will be a linear system for each nuclear geometry R .

The zeroth order approximation to the full molecular wave function is to replace the sum over electronic wave functions by a single term,

$$\Psi_\mathcal{E}(R, r) \approx \psi_i(R, r) \phi_i(R).$$

This is called the *adiabatic approximation*. It amounts to neglecting the coupling between electronic states caused by nuclear motion.

■ Born-Oppenheimer approximation

Using the adiabatic approximation, we can approximate the full molecular Schrödinger equation

$$H \Psi_{\mathcal{E}}(R, r) = \mathcal{E} \Psi_{\mathcal{E}}(R, r)$$

as

$$\begin{aligned} \left(-\frac{\hbar^2}{2} \sum_n \frac{1}{M_n} \nabla_n^2 + H_{\infty} \right) \psi_i(R, r) \phi_i(R) \\ = \left(-\frac{\hbar^2}{2} \sum_n \frac{1}{M_n} \nabla_n^2 + E_i(R) \right) \psi_i(R, r) \phi_i(R) \approx \mathcal{E} \psi_i(R, r) \phi_i(R) \end{aligned}$$

By multiplying both sides of the approximate full molecular Schrödinger equation by the complex conjugate of the electronic wave functions, we get a new Schrödinger equation for the coefficients, $\phi_i(R)$, of the expansion of the full molecular wave function,

$$\left(-\frac{\hbar^2}{2} \sum_n \frac{1}{M_n} \int \psi_i(R, r)^* \nabla_n^2 \psi_i(R, r) dr + E_i(R) \right) \phi_i(R) \approx \mathcal{E} \phi_i(R).$$

▮ Carry out the steps that result in this equation.

This Schrödinger equation is the analogue of the linear systems we have derived previously. It is a single equation, diagonal in i , because of the adiabatic approximation, which, by including only a single term in the expansion of the full molecular wave function, $\Psi_{\mathcal{E}}(R, r)$, disregards all off-diagonal couplings.

This new Schrödinger equation is not algebraic, however, since the first term in brackets is a differential operator, ∇_n^2 , in the coordinates R . The difficulty with this operator is that it has a different form at every position R of the nuclear framework, because of the dependence of the electronic wave function $\psi_i(R, r)$ on the nuclear coordinates.

Since the nuclei are so much more massive than the electrons, it is reasonable to assume that the electronic wave function changes only very slowly as R changes. This assumption is the basis of the *Born-Oppenheimer approximation* which assumes this dependence on R is so weak that first and second derivatives of the electronic wave function with respect to R are negligibly small. With this assumption we can approximate the effect of the differential operator on the coefficients $\phi_i(R)$ as

$$\left(\int \psi_i(R, r)^* \nabla_n^2 \psi_i(R, r) dr \right) \phi_i(R) \approx \left(\int \psi_i(R, r)^* \psi_i(R, r) dr \right) \nabla_n^2 \phi_i(R) = \nabla_n^2 \phi_i(R).$$

▮ Explain why the last step in this expression is justified.

Then the Schrödinger equation for the expansion coefficients $\phi_i(R)$ becomes

$$\left(-\frac{\hbar^2}{2} \sum_n \frac{1}{M_n} \nabla_n^2 + E_i(R) \right) \phi_i(R) \approx \mathcal{E} \phi_i(R).$$

This equation means that the expansion coefficients can be interpreted as the wave functions of nuclear motion taking place on the *potential surface* $E_i(R)$.

■ Summary of the foundation equations of molecular structure

The net result of this analysis is that we determine electronic motion with respect to a fixed nuclear framework, by solving the electronic Schrödinger equation

$$H_{\infty} \psi_i(R, r) = E_i(R) \psi_i(R, r),$$

using the infinite nuclear mass hamiltonian

$$H_{\infty} = -\frac{\hbar^2}{2m} \sum_e \nabla_e^2 + V(R, r).$$

Then we use the adiabatic approximation (that nuclear motion does not couple different electronic states) to express the full molecular wave function as

$$\Psi_{\mathcal{E}}(R, r) \approx \psi_i(R, r) \phi_i(R).$$

Using the Born-Oppenheimer approximation (that the electronic part of this wave function changes only very slowly as the nuclei move) the wave function of nuclear motion is determined by solving the nuclear Schrödinger equation

$$\left(-\frac{\hbar^2}{2} \sum_n \frac{1}{M_n} \nabla_n^2 + E_i(R) \right) \phi_i(R) = \mathcal{E} \phi_i(R).$$

The key feature of this equation is the dependence of the electronic eigenvalue, $E_i(R)$, on nuclear coordinates provide a potential energy for motion of the nuclei.

These four equations form the foundation of the quantum aspects of molecular structure and spectroscopy.