MOLECULES — the Born-Oppenheimer approximation

Molecules are much more difficult than atoms to treat. Two complicating factors:

- No spherical symmetry (there are lower symmetries which we will use)
- Need to calculate motion of electrons <u>and</u> nuclei

The Hamiltonian (i goes over electrons, α over nuclei)

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 - \sum_{\alpha}\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 + V$$

$$V = -\sum_i\sum_\alpha \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_i\sum_{j>i}\frac{e^2}{r_{ij}} + \sum_\alpha\sum_{\beta>\alpha}\frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}}.$$

The Schrödinger equation is

$$H(\vec{r}_i,\vec{R}_\alpha)\Psi(\vec{r}_i,\vec{R}_\alpha) = E\Psi(\vec{r}_i,\vec{R}_\alpha).$$

For convenience, we will denote the various parts of H by T and V,

$$H(\vec{r}_i,\vec{R}_\alpha) = T_e(\vec{r}_i) + T_n(\vec{R}_\alpha) + V_{en}(\vec{r}_i,\vec{R}_\alpha) + V_{ee}(\vec{r}_i) + V_{nn}(\vec{R}_\alpha).$$

These terms represent, in order, the electron kinetic energy, the nuclear kinetic energy, the electron-nuclear attraction, the electron-electron repulsion, and the nuclear-nuclear repulsion.

The first step is the separation of electron and nuclear motion. Since nuclei are 3 orders of magnitude heavier than electrons, the electron "sees" stationary nuclei. The nuclei, on the other hand, see the electrons as a charge distribution, which provides the potential for the nuclear motion. This is the Born-Oppenheimer approximation. As the name implies, the procedure is not exact. However, the errors involved are small in most situations. Moreover, this approach provides a conceptual framework for the discussion of molecular structure.

The molecular Schrödinger equation is solved in two steps:

1. The nuclei are fixed in space, therefore $T_n = 0$ and V_{nn} is a constant. The electronic Hamiltonian is
$$H^e(\vec{r}_i; \vec{R}_\alpha) \equiv T_e(\vec{r}_i) + V_{en}(\vec{r}_i, \vec{R}_\alpha) + V_{ee}(\vec{r}_i) + V_{nn}(\vec{R}_\alpha),$$
and the electronic Schrödinger equation is
$$H^e(\vec{r}_i; \vec{R}_\alpha)\psi^e_\epsilon(\vec{r}_i; \vec{R}_\alpha) = E^e_\epsilon(\vec{R}_\alpha)\psi^e_\epsilon(\vec{r}_i; \vec{R}_\alpha).$$
ϵ denotes the set of electronic quantum numbers. Note that $H^e(\vec{r}_i; \vec{R}_\alpha)$ and $\psi^e_\epsilon(\vec{r}_i; \vec{R}_\alpha)$ are functions of $\vec{r}_i$, but depend parametrically on $\vec{R}_\alpha$, as does E^e_ϵ. This happens because different nuclear coordinates give different electronic Hamiltonians, and therefore different eigenfunctions and eigenvalues. The energy $E^e_\epsilon(\vec{R}_\alpha)$ is the potential surface for the motion of the nuclei in the electronic state ϵ.

2. After the electronic equation has been solved for a variety of molecular configurations, the nuclear Schrödinger equation is solved, using $E^e_\epsilon(\vec{R}_\alpha)$ as the potential surface:
$$H^n_\epsilon(\vec{R}_\alpha) = T_n(\vec{R}_\alpha) + E^e_\epsilon(\vec{R}_\alpha),$$
$$H^n_\epsilon(\vec{R}_\alpha)\psi^n_{\epsilon\nu}(\vec{R}_\alpha) = E_{\epsilon\nu}\psi^n_{\epsilon\nu}(\vec{R}_\alpha).$$
ν is the set of nuclear quantum numbers. The solution of the complete molecular equation is approximated by
$$\Psi_{\epsilon\nu} \approx \psi^e_\epsilon(\vec{r}_i; \vec{R}_\alpha)\psi^n_{\epsilon\nu}(\vec{R}_\alpha),$$

and the energy is close to $E_{\epsilon\nu}$.

For a diatomic molecule, the only internal nuclear coordinate is R_{AB}, and the electronic potential surface is the one-dimensional potential function $E^e(R)$. The solution of the nuclear equation gives a series of vibrational levels (see figure).

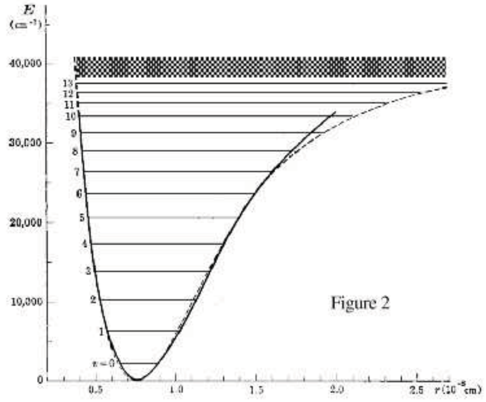


Figure 2

As the name suggests, this is the Born-Oppenheimer approximation. What is the error?

The full molecular Schrödinger equation is

$$(T_e + T_n + V_{en} + V_{ee} + V_{nn})\Psi = E\Psi.$$

The two steps of the solution are

$$(T_e + V_{en} + V_{ee} + V_{nn})\psi^e = E^e\psi^e \quad \text{and} \quad (T_n + E^e) = E\psi^n.$$

If we apply H to $\psi^e\psi^n$, $(T_e + T_n + V_{en} + V_{ee} + V_{nn})\psi^e\psi^n$, ψ^n commutes with all parts of H except T_n, which is the only operator containing derivatives wrt nuclear coordinates. We may therefore write

$$(T_e+T_n+V_{en}+V_{ee}+V_{nn})\psi^e\psi^n = \psi^n(T_e+V_{en}+V_{ee}+V_{nn})\psi^e+T_n\psi^e\psi^n$$

$$= \psi^n E^e\psi^e+\psi^e T_n\psi^n+[T_n,\psi^e]\psi^n = \psi^e(E^e+T_n)\psi^n+[T_n,\psi^e]\psi^n =$$

$$E\psi^e\psi^n + [T_n,\psi^e]\psi^n.$$

The commutator $[T_n, \psi^e]\psi^n$ is added to compensate for putting ψ^n to the left of T_n. If the commutator vanished, the BO approximation would have been exact. Neglecting the commutator amounts to neglecting derivatives of ψ^e wrt nuclear coordinates. Such derivatives appear because ψ^e depends parametrically on R_α. A hand waving argument may be used to show that these derivatives have small effect. ψ^e is expected to depend mainly on electron-nuclear distances, $|r_i - R_\alpha|$. If this is true, the derivatives of ψ^e wrt electronic and nuclear coordinates should be similar, However, derivatives wrt electronic coordinates are multiplied by $\hbar^2/(2m)$, whereas derivatives wrt nuclear coordinates are multiplied by $\hbar^2/(2M_\alpha)$, which is much smaller. This is NOT a rigorous argument, and the situation is more complicated. Nevertheless, The approximation works very well in most cases. Situations where it fails involve crossing of potential surfaces with the same symmetry. In such cases, the crossing point has a degeneracy, which is split by the interaction left out by the approximation, and the shapes and character of the surfaces change significantly.

The simplest molecule – H_2^+

This species is not of great interest in itself, but knowledge gained from its study is applicable to larger, “real” molecules. The Born-Oppenheimer Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R_{AB}},$$

where r_A, r_B are the distances of the electron from nuclei A and B, and R_{AB} is the internuclear separation, treated as a constant when solving the electronic Schrödinger equation. It should be noted that the equation may be separated and solved analytically after transformation to elliptical coordinates ($\xi = \frac{r_A+r_B}{R_{AB}}$, $\eta = \frac{r_A-r_B}{R_{AB}}$, and ϕ is the angle around the z axis as in spherical coordinates). However, this approach is not too helpful for larger molecules, and we will not pursue it.

When the electron is near nucleus A, its behavior is similar to that of an electron in atomic hydrogen, so its wavefunction is close to $1s_A$, or $\sqrt{1/(\pi a_0^3)}e^{-r_A/a_0}$. Obviously, the wavefunction near nucleus B is close to $1s_B$. We can therefore write a simple approximate function for the ground state of H_2^+ in the form $\phi = N(1s_A + 1s_B)$, where N is a normalization factor. ϕ is a molecular orbital, written as a linear combination of atomic orbitals.

N is obtained by requiring normalization:

$$\int \phi^2 d\tau = 1.$$

$$N^2 \int (1s_A + 1s_B)^2 d\tau = 2 + 2S, \quad \text{where} \quad S \equiv \int 1s_A 1s_B d\tau.$$

Therefore $N = \frac{1}{\sqrt{2(1+S)}}$.

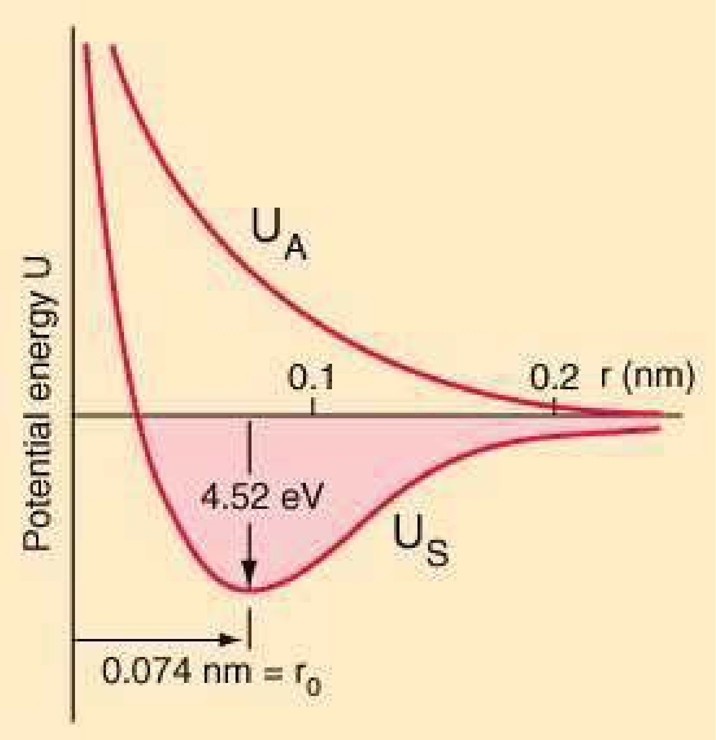
The energy is

$$E = \int \phi H \phi d\tau = \frac{1}{2(1+S)} \left(H_{AA} + H_{AB} + H_{BA} + H_{BB} \right),$$

where the H terms are integrals of the Hamiltonian between atomic orbitals, e.g. $H_{AB} = \int 1s_A H 1s_B d\tau$. Since $H_{AA} = H_{BB}$ and $H_{AB} = H_{BA}$, the result is

$$E = \frac{H_{AA} + H_{AB}}{1+S}.$$

Note that E is a function of the internuclear separation R, which appears as a parameter in the electronic Hamiltonian. If we plot E vs. R, we get a potential curve. An example, showing two curves for H_2, is given here. The lower curve is the H_2 ground state; the upper curve shows an excited, unbound state.



The potential curve is characterized by the position of the minimum (r_e) and the well depth, which is the binding or dissociation energy (D_e). In the example, R$_e$ is 0.074 nm (0.74 Å), and D_e is 4.75 eV (D_0, which takes into account the zero-point energy, is 4.48 eV. The source of the value 4.52 in the picture is not clear). For H_2^+ the values are R_e=1.06 Å, D_e=2.79 eV. The simple function we used gives a qualitatively correct result: the potential has a minimum, indicating the formation of a molecule. However, the values obtained are not satisfactory, with R_e=1.32 Å and D_e=1.77 eV.

How can we improve the results? The first clue is that the calculated R_e is much large than the experimental. This means that our function is biased toward large R. If we look at the limit $R \to \infty$, the system goes into a hydrogen atom (and a far-away proton). The function goes into a H atom $1s$, which is the correct function. At the other limit, $R \to 0$, the system goes into He^+ (we ignore the nuclear repulsion). The wavefunction should then be Ne^{-Zr/a_0}, with Z=2. The variation function we use goes into the same form with Z=1. The natural generalization is to make the exponent a variational parameter, to be optimized separately for every R. The function is then $\phi = N(e^{-\alpha r_A/a_0} + e^{-\alpha r_B/a_0})$, with the variational parameter α. This gives a much better potential, with R_e=1.06 Å and D_e=2.25 eV (α at R_e is 1.23). Thus, R_e agrees with experiment, and the error in D_e went down by $\frac{1}{2}$.

The next improvement involves polarization. The $1s$ orbital has spherical symmetry, which is correct for the free atom but not for the atom in a molecule. The charge is polarized by the other nucleus. There are different ways to allow this effect in the function, but the most widely used method, applicable for larger systems, involves adding orbitals to describe this effect.

In the H_2^+ case, a simple function would be

$$\phi = N[(1s_A + 1s_B) + \lambda(2p_{zA} - 2p_{zB})].$$

Note the minus sign, needed to keep the orbital symmetry. This function, which has 3 parameters (the exponents of $1s$ and $2p_z$ and λ) gives R_e=1.06 Å and D_e=2.73 eV.

The two effects addressed in this improved function are (i) the radial distribution of the electron, determined by the exponent α, and (ii) polarization of the charge, described by the $2p_z$ component. We will see that these two effects are important in larger molecules too.

We have chosen a symmetric combination $1s_A + 1s_B$ as the simplest MO. The antisymmetric combination $1s_A - 1s_B$ also satisfies the requirement of behaving like $1s_A$ near nucleus A and like $1s_B$ near B (it behaves like $-1s_B$, but all observables depend on the square of the function).

Following the same procedure as above, this combination gives

$$\phi_2 = \frac{1}{\sqrt{2(1-S)}}(1s_A - 1s_B); \qquad E_2 = \frac{H_{AA} - H_{AB}}{1-S}.$$

The potential function for E_2 is the upper curve in the diagram showed above. It is a repulsive potential, and a molecule finding itself on this potential dissociates into H+H^+.

The major difference between the two functions may be seen by looking at their charge distributions, and comparing them with the distribution ρ_0 obtained by putting half an electron on A and half on B and ignoring changes caused by molecule formation:

$$\rho_0 = \frac{1}{2}(1s_A^2 + 1s_B^2)$$

$$\rho_1 = |\phi_1|^2 = \frac{1}{2(1+S)}(1s_A^2 + 1s_B^2 + 2 \cdot 1s_A 1s_B)$$

$$\rho_2 = |\phi_2|^2 = \frac{1}{2(1-S)}(1s_A^2 + 1s_B^2 - 2 \cdot 1s_A 1s_B).$$

The density ρ_1 is higher than ρ_0 in the region between the nuclei. ρ_2 is lower in this region, and even vanishes in the plane the points on which are equidistant from the two nuclei, since on this plane $1s_A = 1s_B$ (this plane is a nodal plane).

The property shown here is general. Orbitals which involve increased electron charge between atoms are bonding, contributing to the formation of the molecular bond. Orbitals leading to reduced charge and nodal plane between atoms are antibonding.