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Molecular Orbitals: an Introduction

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A Simple Introduction to Molecular Orbitals

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Separation of variables

We say that a system's Hamiltonian $\hat{H}(q,Q)$ is *separable* if

$$\hat{H}(q,Q) = \hat{H}_q(q) + \hat{H}_Q(Q).$$

If the Hamiltonian of a system is separable, the corresponding energy eigenfunction problem can be broken up into two smaller problems. Explicitly, if

$$\begin{aligned}\hat{H}_q(q)\,\phi_i(q) &= \epsilon_i\,\phi_i(q)\\ \hat{H}_Q(Q)\,\psi_I(Q) &= E_I\,\psi_I(Q)\end{aligned}$$

then

$$\hat{H}(q,Q)\,\phi_i(q)*\psi_I(Q) = (\epsilon_i + E_I)\,\phi_i(q)*\psi_I(Q), \quad \text{all } i, I$$

and the set of functions $\{\phi_i(q)*\psi_I(Q)\}_{i,I}$ provides a basis set for functions of (q,Q). Separable Hamiltonians are easier to diagonalize and the results are easier to comprehend.

The Born-Oppenheimer Approximation

No energy eigenvalue problem for an interesting chemical system can be solved precisely. Thus practical discussions of chemical systems always involve approximations. Usually, the approximation is to treat a system whose Hamiltonian is not separable as if it were separable.

To illustrate this, consider the simplest multi-electron molecule, H_2. If we neglect relativistic corrections, the Hamiltonian for this molecule is

$$\begin{aligned}\hat{H} = &-\frac{\hbar^2}{2M}\left[\frac{\partial^2}{\partial \boldsymbol{R}_1^2}+\frac{\partial^2}{\partial \boldsymbol{R}_2^2}\right]-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial \boldsymbol{r}_1^2}+\frac{\partial^2}{\partial \boldsymbol{r}_2^2}\right]+\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{|\boldsymbol{R}_2-\boldsymbol{R}_1|}+\frac{1}{|\boldsymbol{r}_2-\boldsymbol{r}_1|}\right]\\ &-\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{|\boldsymbol{R}_1-\boldsymbol{r}_1|}+\frac{1}{|\boldsymbol{R}_1-\boldsymbol{r}_2|}+\frac{1}{|\boldsymbol{R}_2-\boldsymbol{r}_1|}+\frac{1}{|\boldsymbol{R}_2-\boldsymbol{r}_2|}\right]\end{aligned} \tag{1}$$

with $\boldsymbol{R}_1, \boldsymbol{R}_2$ locating the nuclei (mass M) and $\boldsymbol{r}_1, \boldsymbol{r}_2$ locating the electrons (mass m). There is a Coulomb interaction between every pair of particles.

With the goal of *separating* this Hamiltonian into an electronic term and a nuclear term, suppose that an energy eigenstate with energy $\mathcal{E}$ has the form

$$\Psi(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{r}_1, \boldsymbol{r}_2) = \Phi(\boldsymbol{R}_1, \boldsymbol{R}_2)\,\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) \tag{2}$$

Then $\hat{H}\,\Psi = \mathcal{E}\,\Psi$ can be rewritten

$$\begin{aligned}&-\frac{\hbar^2}{2m\psi(\boldsymbol{r}_1,\boldsymbol{r}_2)}\left[\frac{\partial^2}{\partial \boldsymbol{r}_1^2}+\frac{\partial^2}{\partial \boldsymbol{r}_2^2}\right]\psi(\boldsymbol{r}_1,\boldsymbol{r}_2)\\ &\qquad+\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{|\boldsymbol{r}_2-\boldsymbol{r}_1|}-\frac{1}{|\boldsymbol{R}_1-\boldsymbol{r}_1|}-\frac{1}{|\boldsymbol{R}_1-\boldsymbol{r}_2|}-\frac{1}{|\boldsymbol{R}_2-\boldsymbol{r}_1|}-\frac{1}{|\boldsymbol{R}_2-\boldsymbol{r}_2|}\right]\\ &\qquad=\frac{\hbar^2}{2M\Phi(\boldsymbol{R}_1,\boldsymbol{R}_2)}\left[\frac{\partial^2}{\partial \boldsymbol{R}_1^2}+\frac{\partial^2}{\partial \boldsymbol{R}_2^2}\right]\Phi(\boldsymbol{R}_1,\boldsymbol{R}_2)-\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\boldsymbol{R}_2-\boldsymbol{R}_1|}+\mathcal{E}\end{aligned} \tag{3}$$

The right hand side of this expression is independent of $\boldsymbol{r}_1, \boldsymbol{r}_2$, but $\boldsymbol{R}_1, \boldsymbol{R}_2$ are present on the left hand side ⇒ A true separation of electronic and nuclear variables has not been achieved. Still, $m \ll M$ leads us to expect that the *motion* of the nuclei will have little effect on the state of the electrons. Essentially, the nuclei provide a constant external field in which the electrons move. Thus we identify an *electronic* Hamiltonian,

$$\begin{aligned}\hat{H}_{elec} = &-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial \boldsymbol{r}_1^2}+\frac{\partial^2}{\partial \boldsymbol{r}_2^2}\right]\\ &+\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_1|}-\frac{1}{|\boldsymbol{R}_2-\boldsymbol{r}_1|}-\frac{1}{|\boldsymbol{R}_1-\boldsymbol{r}_2|}-\frac{1}{|\boldsymbol{R}_2-\boldsymbol{r}_1|}-\frac{1}{|\boldsymbol{R}_2-\boldsymbol{r}_2|}\right],\end{aligned} \tag{4}$$

with the understanding that the eigenvalues and eigenfunctions of $\hat{H}_{elec}$ will depend *parametrically* on $\boldsymbol{R}_1, \boldsymbol{R}_2$,

$$\hat{H}_{elec}\psi_i(\boldsymbol{r}_1, \boldsymbol{r}_2|\boldsymbol{R}_1, \boldsymbol{R}_2) = E_i(\boldsymbol{R}_1, \boldsymbol{R}_2)\psi_i(\boldsymbol{r}_1, \boldsymbol{r}_2|\boldsymbol{R}_1, \boldsymbol{R}_2) \tag{5}$$

With a solution to (5), (3) reduces to

$$-\frac{\hbar^2}{2M}\left[\frac{\partial^2}{\partial \boldsymbol{R}_1^2} + \frac{\partial^2}{\partial \boldsymbol{R}_2^2}\right]\Phi(\boldsymbol{R}_1, \boldsymbol{R}_2) + \left[\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\boldsymbol{R}_2 - \boldsymbol{R}_1|} + E_i(\boldsymbol{R}_2, \boldsymbol{R}_1) - \mathcal{E}\right]\Phi(\boldsymbol{R}_1, \boldsymbol{R}_2) = 0$$

That is, the states of the nuclei are determined by

$$\hat{H}_{nuc}\,\Phi(\boldsymbol{R}_1, \boldsymbol{R}_2) = \mathcal{E}\,\Phi(\boldsymbol{R}_1, \boldsymbol{R}_2)$$

with

$$\hat{H}_{nuc} = -\frac{\hbar^2}{2M}\left[\frac{\partial^2}{\partial \boldsymbol{R}_1^2} + \frac{\partial^2}{\partial \boldsymbol{R}_2^2}\right] + \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\boldsymbol{R}_2 - \boldsymbol{R}_1|} + E_i(\boldsymbol{R}_2, \boldsymbol{R}_1) \tag{6}$$

|| The electronic energy provides a *potential energy* for the nuclear motion. why?

why? Because of the large mass difference between m and M, this separation is usually an excellent approximation. We picture the nuclei as moving (adiabatically) on a *potential energy surface* $E_i(\boldsymbol{R}_2, \boldsymbol{R}_1)$ – the *Born-Oppenheimer* surface* – that is actually the energy of the electrons in the molecule with fixed nuclei. Different Born-Oppenheimer surfaces are associated with different electronic states. Vibrational and rotational spectroscopy is associated with the excitation of *nuclear motion* on a particular Born-Oppenheimer surface. Electronic spectroscopy is associated with transitions between different Born-Oppenheimer surfaces with essentially no nuclear motion.

The Eigenfunctions of $\hat{H}_{elec}$

The only term in $\hat{H}_{elec}$ that prevents us from separating this Hamiltonian into two one-electron Hamiltonians is the electron-electron repulsion term, Coulomb?

$$\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\boldsymbol{r}_2 - \boldsymbol{r}_1|} \tag{7}$$

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* This "almost" separation approximation was introduced by M. Born and J. R. Oppenheimer in 1927.

If we neglect this term, the electronic states of H_2 will have the form

$$\psi_{ij}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \phi_i(\boldsymbol{r}_1)\,\phi_j(\boldsymbol{r}_2) \tag{8}$$

with the $\phi_i(\boldsymbol{r})$ eigenfunctions of the one-electron Hamiltonian

$$\hat{H}_1\,\phi_i(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\nabla^2\,\phi_i(\boldsymbol{r}) - \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{|\boldsymbol{r}-\boldsymbol{R}_1|} + \frac{1}{|\boldsymbol{r}-\boldsymbol{R}_2|}\right]\phi_i(\boldsymbol{r}) = \epsilon_i\,\phi_i(\boldsymbol{r}) \tag{9}$$

The $E_i(\boldsymbol{R}_1,\boldsymbol{R}_2)$ of (5) is now $\epsilon_i + \epsilon_j$. [Keep in mind that $\phi_i(\boldsymbol{r})$ and ϵ_i depend parametrically on $(\boldsymbol{R}_1,\boldsymbol{R}_2)$.] We call the solutions to (9) the *molecular orbitals* (MO's) of H_2. The extension to many electron atoms and molecules is straight-forward.

Note that

1. as the electrons are attracted to the nuclei and repelled by each other, we expect that

   $$\left\langle\frac{1}{|\boldsymbol{r}_2-\boldsymbol{r}_1|}\right\rangle \ll \left\langle\frac{1}{|\boldsymbol{r}_1-\boldsymbol{R}_1|}\right\rangle, \quad \text{etc.}$$

   So the neglect of the term (7) in (4) is not unreasonable. ?

2. the removal of electron-electron interactions destroys any correlation between electrons in different orbitals. This is an approximation that is *qualitatively* unrealistic, even when it is good *quantitatively*. ?

3. less drastic approximations can be made. We'll look at other approximations used to generate molecular orbitals later.

4. (9) can actually be solved exactly for H_2. For any other molecule, however, this is not the case. So the actual determination of molecular orbitals always relies on additional approximations. ?

Molecular Orbitals

All the N-dimensional energy eigenfunction problems for which explicit analytic solutions are known have Hamiltonians that can be "separated" into N one-dimensional problems. It is experience with problems of this special type that forms the basis of our image of real three-dimensional problems.

Multi-electron systems can not be separated in this way, so our experience with solvable problems does not prepare us to deal with multi-electron systems. [If we compute the electronic wave function for the two electrons in H_2, we could only "see" the solution if we were comfortable plotting a function of six variables.] For this reason chemists always approximate real atomic and molecular systems in such a way that a one-particle picture emerges. *Molecular orbitals* are constructed as a first step in trying to describe these systems.

The Hückel Molecular Orbital Theory

As the "π-electrons" in a molecule are less tightly bound than the remaining electrons, they may be approximated as electrons moving independently in a field provided by the remaining charges in the molecule. If there are N atoms in a molecule that contribute a $2p_z$ orbital to the π-system, the π-electron states may be pictured as "linear combinations of atomic orbitals" (LCAO),

$$\psi = \sum_{n=1}^{N} c_n \phi_n. \tag{10}$$

The ϕ_n are "pictured" as $2p_z$ orbitals, but more realistically they are energy eigenstates of an electron moving in the field of the remaining charges of the molecule localized at atom n.

The ψ of (10) describes a single electron. That is, there is an implicit assumption that the Hamiltonian has π-electron contributions that can be separated from all the remaining terms. Such states would be the eigenstates of some one-particle Hamiltonian. Hückel assumed that there was such a Hamiltonian and gave rules for determining this Hamiltonian in the basis set made up of $2p_z$ atomic orbitals: It is simply *assumed* that there is an orthonormal basis set $\{\phi_n\}_{n=1}^{N}$ in which the matrix elements of $\hat{H}$ are

$$H_{ij} = \begin{cases} \alpha & \text{if } i = j, \\ \beta & \text{if } (i, j) \text{ are neighbors,} \\ 0 & \text{otherwise.} \end{cases}$$

Here "α" is the energy of an electron in an isolated ϕ_n state and "β" is a contribution to the energy of an electron from the attraction to nearby nucleus. If a free electron has energy $= 0$, then $\alpha, \beta < 0$.

If $\phi_1, \ldots, \phi_4$ are the local '$2p_z$' orbitals encountered as one moves around the ring in cyclobutadiene, the HMO Hamiltonian for the π electrons in this basis set is

$$H = \begin{bmatrix} \alpha & \beta & 0 & \beta \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ \beta & 0 & \beta & \alpha \end{bmatrix}.$$

The energy eigenvalues are (in ascending order) $\alpha + 2\beta, \alpha, \alpha, \alpha - 2\beta$. The ground state has two electrons with energy $\alpha + 2\beta$ and two with energy α. Spectroscopic excitation requires energy $2|\beta|$.

Rather than try to identify what approximations of the real Hamiltonian lead to separable contributions associated with the π electrons, Hückel simply identified α and β empirically. This was the first *empirical molecular orbital* theory. One finds, for example, a good prediction of the first absorption of a molecule's π-system with

$$\beta = -2.71\text{eV or } -21,900\text{cm}^{-1}$$

Closer comparison with experiment suggests that *different* values for these parameters are required in non-ring structures or in the identification of molecular heats of formation.

An extended Hückel molecular orbital theory

In the mid-1960's, the Hückel model was extended to give a more complete empirical molecular orbital characterization of a molecule. The extension consisted of

1. the inclusion of all *valence* electrons. C_4H_4, for example, is pictured as containing 20 electrons, one from each H-atom and 4 from each C-atom, in atomic orbitals roughly associated with the $1s$ orbital of each H and the $2s, 2p_x, 2p_y$, and $2p_z$ orbitals of each C.

2. the atomic *valence orbitals* are assumed to have a form suggested by J. C. Slater (*Slater type orbitals* or STO's),

$$\psi_{1s}(r) = \frac{\lambda_1^{3/2}}{\pi^{1/2}} e^{-\lambda_1 r} \qquad (H)$$

$$\psi_{2s}(r) = \frac{\lambda_2^{5/2}}{(3\pi)^{1/2}} r\, e^{-\lambda_2 r} \qquad (C)$$

$$\psi_{2p_x}(r) = \frac{\lambda_3^{5/2}}{3\pi^{1/2}} x\, e^{-\lambda_3 r} \qquad (C)$$

$$\cdots \qquad \cdots$$

3. the parameters $\lambda_1, \lambda_2, \lambda_3$ in these atomic orbitals are identified empirically.

4. the one electron Hamiltonian $\hat{H}_1$ is characterized by giving it's matrix representation in the basis set of the valence states. The diagonal matrix elements are just the empirical ionization energies of these orbitals,

   the off-diagonal matrix elements are estimated with

$$H_{ij} = K \frac{H_{ii} + H_{jj}}{2} S_{ij}(R) \quad \text{all } i \neq j,$$

   an estimate originally proposed in 1952 by M. Wolfsberg and L. Helmholtz, with K another empirically determined parameter. $S_{ij}(R)$ is the *overlap integral* between two atomic orbitals,

$$S_{ij} = \int d\boldsymbol{r}\, \phi_i(\boldsymbol{r}) * \phi_j(\boldsymbol{r} - \boldsymbol{R})$$

In this picture, the molecule specific calculation required to construct $\hat{H}_1$ is the evaluation of the overlap integrals. It is the dependence of these integrals on geometry that makes $\hat{H}_1$ vary with geometry. Since the energy of the molecular orbitals depends on geometry, the various Born-Oppenheimer surfaces can be worked out. The *equilibrium* geometry of the ground state is just the configuration with the lowest energy.