Chem 3502/4502 **Physical Chemistry II (Quantum Mechanics)** 3 Credits

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(Some material in this lecture has been adapted from Cramer, C. J. *Essentials of Computational Chemistry*, Wiley, Chichester: 2002; pp. 96-105.)

Recapitulation of the Schrödinger Equation and its Eigenfunctions and Eigenvalues

The operator that returns the system energy, E, as an eigenvalue is called the Hamiltonian operator, H. Thus, we write

$$H\Psi = E\Psi \tag{17-1}$$

which is the Schrödinger equation. The typical form of the Hamiltonian operator with which we will be concerned takes into account five contributions to the total energy of a system (from now on we will say molecule, which certainly includes an atom as a possibility): the kinetic energy of the electrons and nuclei, the attraction of the electrons to the nuclei, and the interelectronic and internuclear repulsions. In more complicated situations, e.g., in the presence of an external electric field, in the presence of an external magnetic field, in the event of significant spin-orbit coupling in heavy elements, taking account of relativistic effects, etc., other terms are required in the Hamiltonian. We will consider some of these at later points, but we will not find them necessary for this lecture. Casting the Hamiltonian into mathematical notation (avoiding atomic units, for the moment, to ensure maximum clarity), we have

$$H = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_k \frac{\hbar^2}{2m_k}\nabla_k^2 - \sum_i \sum_k \frac{e^2 Z_k}{4\pi\varepsilon_0 r_{ik}} + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \sum_{k<l} \frac{e^2 Z_k Z_l}{4\pi\varepsilon_0 r_{kl}} \tag{17-2}$$

where i and j run over electrons, k and l run over nuclei, $\hbar$ is Planck's constant divided by 2π, m_e is the mass of the electron, m_k is the mass of nucleus k, ∇^2 is the Laplacian operator, e is the charge on the electron, Z is an atomic number, $4\pi\varepsilon_0$ is the permittivity of free space, and r_{ab} is the distance between particles a and b. Note that Ψ is thus a function of $3n$ coordinates where n is the total number of particles (nuclei and electrons), e.g., the x, y, and z cartesian coordinates specific to each particle. If we work in cartesian coordinates, the Laplacian has the form

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \tag{17-3}$$

In general, eq. 17-1 has *many* acceptable eigenfunctions Ψ for a given molecule, each characterized by a different associated eigenvalue E. That is, there is a complete set (perhaps infinite) of Ψ_i with eigenvalues E_i. For ease of future manipulation, we may assume without loss of generality that these wave functions are orthonormal, i.e., for a one particle system where the wave function depends on only three coordinates,

$$\iiint \Psi_i^* \Psi_j \, dx\, dy\, dz = \delta_{ij} \tag{17-4}$$

where δ_{ij} is the Kronecker delta (equal to one if $i = j$ and equal to zero otherwise). Orthonormal actually implies two qualities simultaneously: "orthogonal" means that the integral in eq. 17-4 is equal to zero if $i \neq j$ and "normal "means that when $i = j$ the value of the integral is one. For ease of notation, we will henceforth replace all multiple integrals over cartesian space with a single integral over a generalized 3n-dimensional volume element $d\mathbf{r}$, rendering eq. 17-4 as

$$\int \Psi_i^* \Psi_j \, d\mathbf{r} = \delta_{ij} \tag{17-5}$$

Now, consider the result of taking eq. 17-1 for a specific Ψ_i, multiplying on the left by Ψ_j^* and integrating. This process gives

$$\int \Psi_j^* H \Psi_i \, d\mathbf{r} = \int \Psi_j^* E_i \Psi_i \, d\mathbf{r} \tag{17-6}$$

Since the energy E is a scalar value, we may remove it outside the integral on the r.h.s. and use eq. 17-5 to write

$$\int \Psi_j^* H \Psi_i \, d\mathbf{r} = E_i \delta_{ij} \tag{17-7}$$

This equation will prove useful later on, but it is worth noting at this point that it also offers a prescription for determining the molecular energy. With a wave function in hand, one simply constructs and solves the integral on the left (where i and j are identical and index the wave function of interest). Of course, we have not yet said much about the form of the wave function, so the nature of the integral in eq. 17-7 is not obvious . . . although one suspects that it might be decidedly unpleasant to solve in many instances.

The Variational Principle

The power of quantum theory is that if one has a molecular wave function *in hand*, one can calculate physical observables by application of the appropriate operator in a manner analogous to that shown for the Hamiltonian in eq. 17-7. Regrettably, we are occasionally left without a prescription for *obtaining* the orthonormal set of molecular wave functions because the relevant differential equations do not admit to analytic solutions. Let us assume for the moment, however, that we can pick an arbitrary function, Φ, which is indeed a function of the appropriate electronic and nuclear coordinates to be operated upon by the Hamiltonian. Since we defined the set of orthonormal wave functions Ψ_i to be complete (and perhaps infinite), the function Φ must be some linear combination of the Ψ_i, i.e.,

$$\Phi = \sum_i c_i \Psi_i \tag{17-8}$$

where, of course, since we don't yet know the individual Ψ_i, we certainly don't know the coefficients c_i either! Note that the normality of Φ imposes a constraint on the coefficients, however, deriving from

$$\begin{aligned}\int \Phi^* \Phi d\mathbf{r} = 1 &= \int \sum_i c_i^* \Psi_i^* \sum_j c_j \Psi_j d\mathbf{r} \\ &= \sum_{ij} c_i^* c_j \int \Psi_i^* \Psi_j d\mathbf{r} \\ &= \sum_{ij} c_i^* c_j \delta_{ij} \\ &= \sum_i |c_i|^2\end{aligned} \tag{17-9}$$

Now, let us consider evaluating the energy associated with wave function Φ. Taking the approach of multiplying on the left and integrating as outlined above, we have

$$\begin{aligned}\int \Phi^* H \Phi d\mathbf{r} &= \int \left(\sum_i c_i^* \Psi_i^* \right) H \left(\sum_j c_j \Psi_j \right) d\mathbf{r} \\ &= \sum_{ij} c_i^* c_j \int \Psi_i^* H \Psi_j d\mathbf{r} \\ &= \sum_{ij} c_i^* c_j E_j \delta_{ij} \\ &= \sum_i |c_i|^2 E_i\end{aligned} \tag{17-10}$$

where we have used eq. 17-7 to simplify the r.h.s. Thus, the energy associated with the generic wave function Φ is determinable from all of the coefficients c_i (that define how the orthonormal set of Ψ_i combine to form Φ) and their associated energies E_i. Regrettably, we still don't know the values for *any* of these quantities. However, let us take note of the following. In the set of all E_i there must be a lowest energy value (i.e., the set is bounded from below); let us call that energy, corresponding to the "ground state", E_0. [Notice that this boundedness is a critical feature of quantum mechanics! In a classical system, one could imagine always finding a state lower in energy than another state by simply "shrinking the orbits" of the electrons to increase nuclear-electronic attraction while keeping the kinetic energy constant.]

We may now combine the results from eqs. 17-9 and 17-10 to write

$$\int \Phi^* H \Phi d\mathbf{r} - E_0 \int \Phi^* \Phi d\mathbf{r} = \sum_i |c_i|^2 (E_i - E_0) \tag{17-11}$$

As square moduli, each term $|c_i|^2$ must be greater than or equal to zero. By definition of E_0, the quantity $(E_i - E_0)$ must also be greater than or equal to zero. Thus, we have

$$\int \Phi^* H \Phi d\mathbf{r} - E_0 \int \Phi^* \Phi d\mathbf{r} \geq 0 \tag{17-12}$$

which we may rearrange to

$$\frac{\int \Phi^* H \Phi d\mathbf{r}}{\int \Phi^* \Phi d\mathbf{r}} \geq E_0 \tag{17-13}$$

(note that when Φ is normalized, the denominator on the l.h.s. is 1, but it is helpful to have eq. 17-13 in this more general form for future use).

Eq. 17-13 has extremely powerful implications. If we are looking for the best wave function to define the ground state of a system, we can judge the quality of wave functions that we arbitrarily guess by their associated energies, *the lower the better*. This result is critical because it shows us that we don't have to construct our guess wave function Φ as a linear combination of (unknown) orthonormal wave functions Ψ_i, but we may construct it in any manner we wish. The quality of our guess will be determined by how low a value we calculate for the integral in eq. 17-13. Moreover, since we would like to find the lowest possible energy within the constraints of how we go about constructing a wave function, we can use all of the tools that calculus makes available for locating extreme values.

Brief Introduction to the Born-Oppenheimer Approximation

Up to now, we have been discussing many-particle molecular systems entirely in the abstract. In fact, accurate wave functions for such systems are extremely difficult to express because of the correlated motions of particles. That is, the Hamiltonian in eq. 17-2 contains pairwise attraction and repulsion terms, implying that no particle is moving independently of all of the others (the term "correlation" is used to describe this interdependency). In order to simplify the problem somewhat, we may invoke the so-called Born-Oppenheimer approximation. This approximation will be described with more rigor later in the course, but at this point we present the conceptual aspects without delving deeply into the mathematical details.

Under typical physical conditions, the nuclei of molecular systems are moving much, *much* more slowly than the electrons (recall that protons and neutrons are about

1800 times more massive than electrons and note the appearance of mass in the denominator of the kinetic energy terms of the Hamiltonian in eq. 17-2). For practical purposes, electronic "relaxation" with respect to nuclear motion is instantaneous. As such, it is convenient to decouple these two motions, and compute electronic energies for *fixed* nuclear positions. That is, the nuclear kinetic energy term is taken to be independent of the electrons, correlation in the attractive electron-nuclear potential energy term is eliminated, and the repulsive nuclear-nuclear potential energy term becomes a simply evaluated constant for a given geometry. Thus, the *electronic* Schrödinger equation is taken to be

$$\left(H_{\text{el}} + V_N\right)\Psi_{\text{el}}\left(\mathbf{q}_i;\mathbf{q}_k\right) = E_{\text{el}}\Psi_{\text{el}}\left(\mathbf{q}_i;\mathbf{q}_k\right) \tag{17-14}$$

where the subscript "el" emphasizes the invocation of the Born-Oppenheimer approximation, H_{el} includes only the first, third, and fourth terms on the r.h.s. of eq. 17-2, V_N is the nuclear-nuclear repulsion energy, and the electronic coordinates $\mathbf{q}_i$ are independent variables but the nuclear coordinates $\mathbf{q}_k$ are parameters (and thus appear following a semicolon rather than a comma in the variable list for Ψ). The eigenvalue of the electronic Schrödinger equation is called the "electronic energy".

In general, the Born-Oppenheimer assumption is an extremely mild one, and it is entirely justified in most cases. It is worth emphasizing that this approximation has very profound consequences from a conceptual standpoint—so profound that they are rarely thought about but simply accepted as dogma. Without the Born-Oppenheimer approximation we would lack the concept of a potential energy surface: The PES is the surface defined by E_{el} over all possible nuclear coordinates. We would further lack the concepts of equilibrium and transition state geometries, since these are defined as critical points on the PES; instead we would be reduced to discussing high-probability regions of the nuclear wave functions. Of course, for some problems in Chemistry, we *do* need to consider the quantum mechanical character of the nuclei, but the advantages afforded by the Born-Oppenheimer approximation should be manifest.

Construction of Trial Wave Functions: LCAO Basis Set Approach

Eq. 17-14 is simpler than eq. 17-1 because electron-nuclear correlation has been removed. The remaining correlation, that between the individual electrons, is considerably more troubling. For the moment we will take the simplest possible approach and ignore it; we do this by considering systems with only a single electron. The electronic wave function has thus been reduced to depending only on the fixed nuclear coordinates and the three cartesian coordinates of the single electron. The eigenfunctions of eq. 17-14 for a molecular system may now be properly called molecular orbitals (MOs; rather unusual ones in general, since they are for a molecule having only one electron, but MOs nonetheless). To distinguish a one-electron wave function from a many-electron wave function, we will designate the former as ψ_{el} and the latter as Ψ_{el}.

We will hereafter drop the subscript "el" where not required for clarity; unless otherwise specified, all wave functions are electronic wave functions.

The pure electronic energy eigenvalue associated with each molecular orbital is the energy of the electron in that orbital. Experimentally, one might determine this energy by measuring the ionization potential of the electron when it occupies the orbital (fairly easy for the hydrogen atom, considerably more difficult for polynuclear molecules). To measure E_{el}, which includes the nuclear repulsion energy, one would need to determine the "atomization" energy, that is, the energy required to ionize the electron *and* to remove all of the nuclei to infinite separation. In practice, atomization energies are not measured, but instead we have compilations of such thermodynamic variables as heats of formation. The relationship between these computed and thermodynamic quantities will be discussed in more detail later in the course.

As noted above, we may imagine constructing wave functions in any fashion we deem reasonable, and we may judge the quality of our wave functions (in comparison to one another) by evaluation of the energy eigenvalues associated with each. The one with the lowest energy will be the most accurate and presumably the best one to use for computing other properties by the application of other operators. So, how might one go about choosing mathematical functions with which to construct a trial wave function? This is a typical question in mathematics—how can an arbitrary function be represented by a combination of more convenient functions? The convenient functions are called a "basis set". Indeed, we have already encountered this formalism—we used power series as polynomial basis sets for harmonic oscillator and hydrogenic wave functions.

In our QM systems, we have temporarily restricted ourselves to systems of one electron. If, in addition, our system were to have only one nucleus, then we would not need to guess wave functions, but instead we could solve eq. 17-14 *exactly*. The eigenfunctions that are determined in that instance are the familiar hydrogenic atomic orbitals, 1s, 2s, 2p, 3s, 3p, 3d, etc., whose properties and derivation we've already discussed in detail. We now posit that, as functions, they may be useful in the construction of more complicated *molecular* orbitals. In particular, just as in eq. 17-8 we constructed a guess wave function as a linear combination of exact wave functions, so here we will construct a guess wave function ϕ as a linear combination of *atomic* wave functions φ, i.e.,

$$\phi = \sum_{i=1}^{N} a_i \varphi_i \tag{17-15}$$

where the set of N functions φ_i is called the "basis set" and each has associated with it some coefficient a_i. This construction is known as the linear combination of atomic orbitals (LCAO) approach.

Note that eq. 17-15 does not specify the locations of the basis functions. Our intuition suggests that they should be centered on the atoms of the molecule, but this is certainly not a requirement. If this comment seems odd, it is worth emphasizing at this point that we should not let our chemical intuition limit our mathematical flexibility. As chemists, we choose to use atomic orbitals (AOs) because we anticipate that they will be efficient functions for the representation of MOs. However, as mathematicians, we should immediately stop thinking about our choices as orbitals, and instead consider them only to be *functions*, so that we avoid being conceptually influenced about how and where to use them.

Recall that the wave function squared has units of probability density. In essence, the electronic wave function is a road map of where the electrons are more or less likely to be found. Thus, we want our basis functions to provide us with the flexibility to allow electrons to "go" where their presence at higher density lowers the energy. For instance, to describe the bonding of a hydrogen atom to a carbon, it is clearly desirable to use a p function on hydrogen, oriented along the axis of the bond, to permit electron density to be localized in the bonding region more efficiently than is possible with only a spherically symmetric s function. Does this imply that the hydrogen atom is somehow sp-hybridized? Not necessarily—the p function is simply serving the purpose of increasing the flexibility with which the *molecular* orbital may be described. If we took away the hydrogen p function and instead placed an s function *in between* the C and H atoms, we could also build up electron density in the bonding region.

One should also note that the summation in equation 17-15 has an upper limit *N*; we can not work with an infinite basis in any convenient way (at least not when the basis is AOs). However, the more atomic orbitals we allow into our basis, the closer our basis will come to "spanning" the true molecular orbital space. Thus, the chemical idea that we would limit ourselves to, say, at most one 1s function on each hydrogen atom is needlessly confining from a mathematical standpoint. Indeed, there may be very many "true" one-electron MOs that are very high in energy. Accurately describing these MOs may require some unusual basis functions, e.g., very diffuse functions to describe weakly bound electrons, like those found in so-called Rydberg states.

All that being said, let us now turn to evaluating the energy of our guess wave function. From eqs. 17-13 and 17-15 we have

$$
\begin{aligned}
E &= \frac{\int\left(\sum_i a_i^* \varphi_i^*\right) H \left(\sum_j a_j \varphi_j\right) d\mathbf{r}}{\int\left(\sum_i a_i^* \varphi_i^*\right)\left(\sum_j a_j \varphi_j\right) d\mathbf{r}} \\
&= \frac{\sum_{ij} a_i^* a_j \int \varphi_i^* H \varphi_j d\mathbf{r}}{\sum_{ij} a_i^* a_j \int \varphi_i^* \varphi_j d\mathbf{r}} \\
&= \frac{\sum_{ij} a_i^* a_j H_{ij}}{\sum_{ij} a_i^* a_j S_{ij}}
\end{aligned}
\quad . \tag{17-16}
$$

where we have introduced the shorthand notation H_{ij} and S_{ij} for the integrals in the numerator and denominator, respectively. These so-called "matrix elements" are no longer as simple as they were in prior discussion, since the atomic orbital basis set, while likely to be efficient, is no longer likely to be orthonormal. These matrix elements have more common names: H_{ij} is called a "resonance integral", and S_{ij} is called an "overlap integral". The latter has a very clear physical meaning, namely the extent to which any two basis functions overlap in a phase-matched fashion in space. The former integral is not so easily made intuitive, but it is worth pointing out that orbitals which give rise to large overlap integrals will similarly give rise to large resonance integrals. One resonance integral which *is* intuitive is H_{ii}, which corresponds to the energy of a single electron occupying basis function i, i.e., it is essentially equivalent to the ionization potential of the AO in the environment of the surrounding molecule.

Now, it is useful to keep in mind our objective. The variational principle instructs us that as we get closer and closer to the "true" one-electron ground-state wave function, we will obtain lower and lower energies from our guess. Thus, once we have selected a basis set, we would like to choose the coefficients a_i so as to *minimize* the energy for all possible linear combinations of our basis functions. From calculus, we know that a necessary condition for a function (i.e., the energy) to be at its minimum is that its derivatives with respect to all of its free variables (i.e., the coefficients a_i) are zero. Notationally, that is

$$
\frac{\partial E}{\partial a_k} = 0 \quad \forall\ k \tag{17-17}
$$

(where we make use of the mathematical abbreviation ∀ meaning "for all"). Performing this fairly tedious partial differentiation on equation 17-16 for each of the N variables a_k gives rise to N equations which must be satisfied in order for equation 17-17 to hold true, namely

$$\sum_{i=1}^{N} a_i\left(H_{ki} - ES_{ki}\right) = 0 \quad \forall\ k\,. \tag{17-18}$$

This set of N equations (running over k) involves N unknowns (the individual a_i values). From linear algebra, we know that a set of N equations in N unknowns has a non-trivial solution if and only if the determinant formed from the coefficients of the unknowns (in this case the "coefficients" are the various quantities $H_{ki} – ES_{ki}$) is equal to zero. Notationally again, that is

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0 \tag{17-19}$$

Equation 17-19 is called a secular equation. In general, there will be N roots E which permit the secular equation to be true. That is, there will be N energies E_j (some of which may be equal to one another, in which case we say the roots are "degenerate") where each value of E_j will give rise to a different set of coefficients, a_{ij}, which can be found by solving the set of linear equations 17-18 using that specific E_j, and these coefficients will define an optimal associated wave function ϕ_j within the given basis set, i.e.,

$$\phi_j = \sum_{i=1}^{N} a_{ij}\varphi_i\,. \tag{17-20}$$

In a one-electron system, the lowest energy molecular orbital would thus define the "ground state" of the system, and the higher energy orbitals would be "excited states". Obviously, as these are different MOs, they have different basis function coefficients. Although we have not formally proven it, it is worth noting that the variational principle holds for the excited states as well: the calculated energy of a guess wave function for an excited state will be bounded from below by the true excited state energy.

So, in a nutshell, to find the optimal one-electron wave functions for a molecular system, we:

(1) Select a set of N basis functions.

(2) For that set of basis functions, determine all N^2 values of both H_{ij} and S_{ij}.

(3) Form the secular determinant, and determine the N roots E_j of the secular equation.

(4) For each of the N values of E_j, solve the set of linear eqs. 17-18 in order to determine the basis set coefficients a_{ij} for that MO.

All of the MOs determined by this process are mutually orthogonal (because they are eigenfunctions of a Hermitian operator). For degenerate MOs, some minor complications arise, as always, but those are not discussed here.

Homework

To be solved in class:

A quantum-mechanical system is known to have an *approximate* energy given by $\langle H \rangle = 3a^4 - 4a^3 - 36a^2 + 10$ where a is a variational parameter. What is the highest energy that the actual system can possibly have in its ground state? (Don't be fooled by the way the question is phrased—involving the "highest energy"—the question involves the ground state, and the variational principle tells us about bounds on the ground-state energy.)

To be turned in for possible grading Mar. 10:

None. Relax in the wake of the second exam.