

APPROXIMATE SOLUTIONS TO THE MOLECULAR HAMILTONIAN

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In this course, we are concerned with determining the energy and wave function for a given molecule or molecular system. Given any molecule comprised of M nuclei and N electrons, the time-independent Schrödinger equation takes the form

$$\hat{H}|\Psi\rangle = \mathcal{E}|\Psi\rangle \quad (1)$$

where \hat{H} is the Hamiltonian which describes the molecules/system of interest:

$$\hat{H} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2m_A} \nabla_A^2 - \sum_{i,A=1}^{N,M} \frac{Z_A}{r_{iA}} + \frac{1}{2} \sum_{ij}^N \frac{1}{r_{ij}} + \frac{1}{2} \sum_{AB}^M \frac{Z_A Z_B}{R_{AB}} \quad (2)$$

Here, m_A is the mass of nuclei A , Z_A is the charge of nuclei A , and r_{ij} , r_{iA} , R_{AB} is the electron-electron distance, electron-nuclei distance, and nuclei-nuclei distance respectively. Unfortunately, for any realistic system of interest (ie more than 1 electron, as we will see), this becomes intractable to solve exactly. Instead we have to turn to using various approximations to solve Eq. (1). The problem hence lies in, what approximations can we make. And given an approximate solution, how can I get a better approximation?

We will first discuss the variational principle which guides in assess the quality of our approximate solutions and how to get an optimal solution from a guess wave function. Then, we will consider the Born-Oppenheimer approximation and when it is a valid approximation.

1. BRIEF QUANTUM MECHANICS REVIEW

The Hamiltonian is a Hermitian operator. We will assume for simplicity that it has at most a countable number of eigenvectors (though, it is possible that Hamiltonians have a continuum of eigenstates, consider the free particle). Lets enumerate the eigenstates $|\Phi_\alpha\rangle$ and their corresponding energies \mathcal{E}_α . Now, since \hat{H} is Hermitian, the eigenvalues \mathcal{E}_α are real-valued so that we can order the states/energies such that

$$\mathcal{E}_\alpha \leq \mathcal{E}_{\alpha+1} \quad (3)$$

We denote $|\Phi_0\rangle$ the ground-state wave function and \mathcal{E}_0 the corresponding ground-state energy. Furthermore, we know that the eigenvectors are orthonormal to one another:

$$\langle \Phi_\alpha | \Phi_\beta \rangle = \delta_{\alpha\beta} \quad (4)$$

Additionally, for any wave function $|\Psi\rangle$ in the Hilbert space defined by \hat{H} can be expanded as a linear combination of the eigenstates by inserting the resolution of the identity.

$$|\Psi\rangle = \sum_{\alpha} c_{\alpha} |\Phi_{\alpha}\rangle \quad (5)$$

$$c_\alpha = \langle \Phi_\alpha | \Psi \rangle \quad (6)$$

2. THE VARIATIONAL PRINCIPLE

Given any approximate wave function for the ground state of our system, is there any way to say how close the energy is to the true ground-state energy? The variational theorem actually tells us that the energy of the approximate wave function is an upper-bound for the true ground-state energy!

Theorem 1 (The Variational Principle). Given a normalized wave function $|\Psi\rangle$ that satisfies the boundary conditions, then

$$\mathcal{E}_0 \leq \langle \Psi | \hat{H} | \Psi \rangle \quad (7)$$

The equality holds if and only if $|\Psi\rangle = |\Phi_0\rangle$.

Proof. Since $|\Psi\rangle$ is normalized, then we must have that

$$\sum_\alpha |c_\alpha|^2 = 1 \quad (8)$$

We therefore begin writing that

$$\langle \Psi | \hat{H} | \Psi \rangle = \sum_\alpha \mathcal{E}_\alpha |c_\alpha|^2 \quad (9)$$

Noting that $\mathcal{E}_0 \leq \mathcal{E}_\alpha$ for all α , then we must have that

$$\mathcal{E}_0 = \mathcal{E}_0 \sum_\alpha |c_\alpha|^2 \leq \sum_\alpha \mathcal{E}_\alpha |c_\alpha|^2 \quad (10)$$

Trivial to see that equality holds if and only if $|\Psi\rangle = |\Phi_0\rangle$. \square

Any approximate wave function will always have an energy that is too high as compared to the ground state. We can then improve our wave function by minimizing the energy. In fact, we can write that the ground-state energy is the minimum energy of any normalized wave function.

$$\mathcal{E}_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle, \text{ where } \langle \Psi | \Psi \rangle = 1 \quad (11)$$

One can of course show that for some unnormalized wave function $|\psi\rangle$, the variational principle can be written as

$$\frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \geq \mathcal{E}_0 \quad (12)$$

The variational parameter also tells us how to tune our wave function guesses to get better approximate solutions to the ground-state energy and wave function. That is, given some trial wave function which depends on some continuous parameters $\vec{\lambda}$, $|\Psi(\vec{\lambda})\rangle$, then our variational estimate to the true ground-state energy can be achieved by minimizing $\langle \Psi(\vec{\lambda}) | \hat{H} | \Psi(\vec{\lambda}) \rangle$ with respect to the parameters $\vec{\lambda}$.

Example 2. Lets consider one of the simplest systems: a particle in a box of length $L = 1$. If we assume the particle has a mass of 1 a.u., then the exact ground-state wave function is

$$\psi_0(x) = \sqrt{2} \sin(\pi x) \quad (13)$$

for $x \in [0, 1]$ and with an energy of

$$\mathcal{E}_0 = \frac{\pi^2}{2} \quad (14)$$

Lets imagine we didn't know how to solve this problem. Based off of the boundary conditions, we expect the wave function to be 0 at both ends of the box. A very simple guess of the wave function is thus

$$\psi(x) = x(1 - x) \quad (15)$$

This has the correct behavior at $x = 0, 1$. However, there is no parameter which we could introduce to variationally optimize. One such parameter that we could add though is

$$\xi(x, \alpha) = x^\alpha(1 - x) \quad (16)$$

Of course, we need to normalize this trial wave function, so we consider

$$\begin{aligned} \langle \xi | \xi \rangle &= \int_0^1 dx x^{2\alpha} (1 - x)^2 \\ &= \int_0^1 dx (x^{2\alpha} - 2x^{2\alpha+1} + x^{2\alpha+2}) \\ &= \frac{1}{2\alpha + 1} - \frac{2}{2\alpha + 2} + \frac{1}{2\alpha + 3} \\ &= \frac{2}{(2\alpha + 1)(2\alpha + 2)(2\alpha + 3)} \end{aligned} \quad (17)$$

If we then consider the expectation value of \hat{H} , we have

$$\langle \xi | \hat{H} | \xi \rangle = \int_0^1 dx x^\alpha (1 - x) \left(-\frac{1}{2} \frac{d^2}{dx^2} \right) (x^\alpha (1 - x)) \quad (18)$$

The second derivative of $\xi(x, \alpha)$ is given by

$$\begin{aligned} \frac{d^2}{dx^2} \xi(x, \alpha) &= \frac{d}{dx} (\alpha x^{\alpha-1} (1 - x) - x^\alpha) \\ &= \alpha(\alpha - 1)x^{\alpha-2}(1 - x) - \alpha x^{\alpha-1} - \alpha x^{\alpha-1} \\ &= (\alpha^2 - \alpha)x^{\alpha-2} - (\alpha^2 + \alpha)x^{\alpha-1} \end{aligned} \quad (19)$$

Inserting this into Eq. (18), we get

$$\begin{aligned} \langle \xi | \hat{H} | \xi \rangle &= -\frac{\alpha}{2} \int_0^1 dx ((\alpha - 1)x^{2\alpha-2} - 2\alpha x^{2\alpha-1} + (\alpha + 1)x^{2\alpha}) \\ &= -\frac{\alpha}{2} \left(\frac{\alpha - 1}{2\alpha - 1} - 1 + \frac{\alpha + 1}{2\alpha + 1} \right) \\ &= \frac{\alpha}{2(2\alpha - 1)(2\alpha + 1)} \end{aligned} \quad (20)$$

Hence, our energy for $|\xi\rangle$ can be expressed as a function of α as

$$\mathcal{E}(\alpha) = \frac{2\alpha^3 + 5\alpha^2 + 3\alpha}{4\alpha - 2} \quad (21)$$

Now, we find our optimal value of α when the derivative is zero, so we solve now

$$\begin{aligned} 0 &= \frac{d}{d\alpha} \mathcal{E}(\alpha) \\ &= \frac{(6\alpha^2 + 10\alpha + 3)(4\alpha - 2) - 4(2\alpha^3 + 5\alpha^2 + 3\alpha)}{(4\alpha - 2)^2} \\ &= \frac{16\alpha^3 + 8\alpha^2 - 20\alpha - 6}{16\alpha^2 - 16\alpha + 4} \end{aligned} \quad (22)$$

We hence need to find the zeros to the polynomial equations

$$16\alpha^3 + 8\alpha^2 - 20\alpha - 6 \quad (23)$$

Numerically solving this, we find that the appropriate value of α is $\alpha_0 = 1.043$ (and we check that the numerator is also not 0). We can then calculate our energy for the state $\xi(x, \alpha_0)$ by

$$\mathcal{E}(\alpha_0) = 4.99 \quad (24)$$

How does this compare to the exact result? Well the exact result is approximately 4.93 a.u., so we have an error of just a bit over 1%.

However, we should note that our variational wave function does not obey the symmetry of the system! If one computes $\langle \xi, \alpha_0 | \hat{X} | \xi, \alpha_0 \rangle$, we find the value to be $0.507 \neq 0.5$. That is, it slightly biases one side of the box over the other, when *a priori* this should not be the case. In fact, if we were to enforce symmetry on our final wave function, it would require that $\alpha = 1$. We could of course relax this by considering the symmetry-adapted trial wave function

$$\xi(x, \alpha) = x^\alpha (1 - x^\alpha) \quad (25)$$

and solving. This would give the correct spatial symmetry for the wave function, though it does not necessarily guarantee a more accurate energy! It therefore should be noted that the variational principle does not converge to a solution which preserves the symmetry of the Hamiltonian, this information has to be encoded within the trial wave function!

Once a bound has been obtained, we can estimate the quality by considering a trial function with more parameters. If this produced a substantially lower upper bound, we keep going. But, if we feel “resistance” and we cannot make any substantial improvement, then we may begin to suspect that \mathcal{E}_0 is not too far below.

Example 3. Lets consider the hydrogen atom. The Hamiltonian takes the form

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r} \quad (26)$$

We know that the ground state energy (in atomic units) is $-\frac{1}{2}$ and the ground state wave function is

$$\psi(r) = \frac{1}{\sqrt{\pi}} e^{-r} \quad (27)$$

Lets assume we didn't know this though. We would again suspect our ground-state wave function is spherically symmetric and should decay as $r \rightarrow \infty$. If we want simple integrals, the Gaussian is again a great choice.

We again can find the energy as a function of α as

$$\mathcal{E}(\alpha) = \frac{3\alpha}{2} - 2\left(\frac{2\alpha}{\pi}\right)^{1/2} \quad (28)$$

Finding the optimal value of α , we get

$$\alpha_0 = \frac{8}{9\pi} \quad (29)$$

$$\mathcal{E}(\alpha_0) = -\frac{4}{3\pi} \approx -0.424 \quad (30)$$

As we can see, we are not too far off from the actual ground-state energy! Only about 0.75 Hartree's.

Example 4. Here, we are concerned with the ground state of He. Lets ignore nuclear motion so that our Hamiltonian in the coordinate basis is

$$H(r_1, r_2) = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \quad (31)$$

where r_1, r_2 are the radial coordinates of electron 1 and 2, and r_{12} is the radial separation between the electrons. If we ignored electron-electron repulsion terms, then our Hamiltonian is separable and we know the ground-state wave function (ignoring spin) is

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) \quad (32)$$

Here, $\psi_{100}(\mathbf{r}_1)$ is the Hydrogen-like ground-state wave function but with a slightly higher charged nucleus (which depends on say Z).

$$\psi_{100}(\mathbf{r}) = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr} \quad (33)$$

In the specific case of He, $Z = 2$. Hence, our wave function under the assumption the electrons do not interact is given by

$$\psi = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)} \quad (34)$$

Additionally, the energy for this crude approximation is given by

$$\mathcal{E} = -4 \text{ a.u.} \approx -108.8 \text{ eV} \quad (35)$$

The experimentally measured value is -78.6 eV for the He, hence we are fairly far off. In general, omitting the electron-electron repulsion term is bad; however, if we keep it, we cannot solve the problem analytically. Instead, lets turn to the variational principle to get an upper bound. For a trial wave function, lets take our product form Eq. (34), but treat Z now as a variable. The physical motivation for this is that the other electron screens some of the nuclear charge for the other electron creating an effective Z that should be less than 2. If we perform the calculation for the energy

$$\mathcal{E}(Z) = -\left(4Z - Z^2 - \frac{5}{8}Z\right) \quad (36)$$

Solving for the optimal Z , we find that it is not at 2, but instead at $Z = 2 - \frac{5}{16}$ with a corresponding energy of

$$\mathcal{E}(2 - \frac{5}{16}) \approx -77.5 \text{ eV} \quad (37)$$

This is much closer to the real, experimentally determined answer! Furthermore, our approximate answer lies above the true ground state (which is required by the variational principle). Of course, one can try other trial functions with more and more parameters, and they will get a little lower, but they will also meet the “resistance” to further lowering.

3. THE BORN-OPPENHEIMER APPROXIMATION

The full molecular Hamiltonian takes the form

$$\hat{H}^{\text{mol}} = \hat{T}^{\text{el}} + \hat{T}^{\text{nuc}} + \hat{V}^{\text{el}} + \hat{V}^{\text{nuc}} + \hat{V}^{\text{nuc,el}} \quad (38)$$

where \hat{T} is the kinetic energy operator and \hat{V} describes the interaction between the various particles. Now, because the mass of nuclei are much heavier than electrons, they move much slower. Hence, to a good approximation, as the nuclei are moving, the electrons effectively see a static field of point charges since they are able to reorganize and respond to a change in the nuclei much faster than the nuclei are moving. This is the fundamental motivation for the Born-Oppenheimer approximation which allows us to separate the nuclear and electronic degrees of freedom.

Under this assumption, we can write down the electronic Hamiltonian as just

$$\hat{H}^{\text{el}} = \hat{T}^{\text{el}} + \hat{V}^{\text{nuc,el}} + \hat{V}^{\text{el}} \quad (39)$$

Note that V^{nuc} is just a constant and so the eigenvectors for \hat{H}^{el} do not depend on it, hence we omit it when solving for the eigenvectors. Solutions to the electronic Hamiltonian take the form $|\Phi^{\text{el}}; \mathbf{R}\rangle$

$$\hat{H}^{\text{el}} |\Phi^{\text{el}}; \mathbf{R}\rangle = \mathcal{E}^{\text{el}}(\mathbf{R}) |\Phi^{\text{el}}; \mathbf{R}\rangle \quad (40)$$

and they and their corresponding eigenvalues depend parametrically on the nuclear coordinates. We will drop this implicit dependence on \mathbf{R} for simplicity. The total energy is then the sum of electronic and nuclear-nuclear interaction energy

$$\mathcal{E}^{\text{tot}} = \mathcal{E}^{\text{el}} + \sum_{A \neq B} \frac{Z_A Z_B}{R_{AB}} \quad (41)$$

Here, we have that Z_A is the charge of nuclei A and R_{AB} is the internuclear distance between atom A and B . It is then possible to solve for the nuclear degrees of freedom in a similar way which gives rise to the nuclear Schrödinger equation. This gives rise to vibrational, rotational, and translational energy. For this course, we focus sole on the electronic problem and will drop the el subscripts unless necessary to distinguish.

4. LINEAR VARIATIONAL METHOD: LCAO BASIS SET APPROACH

While we have simplified the form of our Hamiltonian substantially by removing the electron-nuclear correlation, we still have to deal with the electron-electron correlation. Lets, for now, just ignore it, or only consider a single electron in some field of point charges. The corresponding eigenfunctions we would call molecular orbitals (MO) and the energy would be the orbital energy.

Our question then is, how can we best approximate our single particle wave function (or MO)? Well for a single nuclei and single electron, we can solve this exactly and get the corresponding hydrogenic atomic orbitals: 1s, 2s, 2p, etc. Using chemical and physical intuition, it makes sense then to approximate the molecular orbital as a linear combination of atomic orbitals.

We start with the following set of atomic orbitals $|\phi_\mu\rangle$. Each AO is centered on some particular nuclei (and is the exact wave function for the corresponding electronic Hamiltonian). It should be obvious that

$$\langle\phi_\mu|\phi_\nu\rangle = S_{\mu\nu} \neq \delta_{\mu\nu} \quad (42)$$

generally speaking. Though of course for 2 AOs centered on the same nuclei, this is necessarily the case. We therefore approximate our ground-state MO as

$$|\phi\rangle = \sum_{\mu=1}^N c_\mu |\phi_\mu\rangle \quad (43)$$

Here, we call $|\phi_\mu\rangle$ our basis set, and in particular, this expansion is commonly known as the linear combination of atomic orbitals (LCAO). Now, it should be seen that I have limited our basis set to some N functions. Mathematically, we can always handle an infinite (countable or uncountable) basis functions, but in practice we would have trouble with even a countable infinite number of basis functions. Of course, as $N \rightarrow \infty$, our approximate wave function and energy will approach the basis set limit.

Now, our wave function should be normalized so that

$$\langle\phi|\phi\rangle = \sum_{\mu\nu} c_\mu^* S_{\mu\nu} c_\nu = 1 \quad (44)$$

If we assume we have properly normalized our wave function, then the energy is given by

$$\begin{aligned} \mathcal{E}(\mathbf{c}) &= \langle\phi|\hat{H}|\phi\rangle = \sum_{\mu\nu} c_\mu^* \langle\phi_\mu|\hat{H}|\phi_\nu\rangle c_\nu \\ &= \sum_{\mu\nu} c_\mu^* H_{\mu\nu} c_\nu \end{aligned} \quad (45)$$

As can be seen, our free parameters are \mathbf{c} . The variational method says then that our best approximation to the energy and wave function is by setting

$$\forall \mu, \frac{\partial \mathcal{E}}{\partial c_\mu} = 0 \quad (46)$$

However, we must optimize with the constraint that $\langle\phi|\phi\rangle = 1$! Therefore, we must use Lagrange's method of Undetermined multipliers. We proceed by defining the Lagrangian as

$$\mathcal{L}(\mathbf{c}) = \mathcal{E}(\mathbf{c}) - E(\langle\phi|\phi\rangle - 1) \quad (47)$$

Here E is the Lagrange multiplier term which is allowed to vary freely. Notice that we have essentially added 0 to the energy equation! It is known then that the minimum of

$\mathcal{E}(\mathbf{c})$ given the constraint $\langle \phi | \phi \rangle = 1$ is achieved at the same minimum as $\mathcal{L}(\mathbf{c})$. Hence, taking the derivative with respect to c_η we obtain

$$\begin{aligned} \frac{\partial \mathcal{L}(\mathbf{c})}{\partial c_\eta} &= \frac{\partial}{\partial c_\eta} \sum_{\mu\nu} c_\mu^* H_{\mu\nu} c_\nu - E \frac{\partial}{\partial c_\eta} \sum_{\mu\nu} c_\mu^* S_{\mu\nu} c_\nu \\ &= \sum_\nu H_{\eta\nu} c_\nu + \sum_\mu c_\mu^* H_{\mu\eta} - E \left(\sum_\nu S_{\eta\nu} c_\nu + \sum_\mu c_\mu^* S_{\mu\eta} \right) \\ &= 2 \sum_\nu H_{\eta\nu} c_\nu - 2E \sum_\nu S_{\eta\nu} c_\nu \end{aligned} \quad (48)$$

Hence, we are optimized when, $\forall c_\eta$,

$$\sum_\nu H_{\eta\nu} c_\nu = E \sum_\nu S_{\eta\nu} c_\nu \quad (49)$$

and this can be rewritten in matrix form as

$$\mathbf{H}\mathbf{c} = E\mathbf{S}\mathbf{c} \quad (50)$$

Of course though, this will have N possible solutions \mathbf{c}_i yielding N different wave functions $|\phi_i\rangle$, and N different E which we label E_i . If we take Eq. (49) and multiply by $c_{i\mu}^*$ on the right, we obtain

$$\sum_{\mu\nu} c_{i\mu}^* H_{\mu\nu} c_{i\nu} = E_i \sum_{\mu\nu} c_{i\mu}^* S_{\mu\nu} c_{i\nu} \quad (51)$$

But this simplifies to

$$\langle \phi_i | \hat{H} | \phi_i \rangle = E_i \quad (52)$$

So the eigenvalues are exactly our approximate energies! So in one shot, we have found the first N approximate eigenstates given the basis set $|\phi_\mu\rangle$.

Essentially then, to find the optimal one-electron wave function for a molecular system, we

- (1) Select a set of N basis functions.
- (2) For that set of basis functions, determine all values of $H_{\mu\nu}$ and $S_{\mu\nu}$.
- (3) Solve the generalized eigenvalue equations of Eq. (50) to get the basis set coefficients $c_{i\mu}$.