

Week 5

Approximate Solutions of the Schrödinger Equation

5.1 Approximation Methods

10/25:

- The **variational method** and **perturbation theory** are two methods of approximating solutions to Schrödinger equations describing systems more complex than the hydrogen atom.

- To begin our investigation of the variational method, we will look at the particle in a box.

- Consider a Hamiltonian for an electron in a box of length $L = 2$ a.u. centered around $x = 0$.

- Note that we take the electron as the fundamental mass, \hbar as the fundamental unit of energy time, and the charge of the electron as the fundamental unit of charge, and the Bohr radius as the fundamental unit of length.

- Our Hamiltonian is

$$H\psi(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x)$$

or, in atomic units,

$$H\psi(x) = -\frac{1}{2} \frac{d^2}{dx^2} \psi(x)$$

- **Variational theorem:** The expectation value of our Hamiltonian with respect to a trial wave function produces an approximate energy. Moreover^[1],

$$E_{\text{approx}} \geq E_{\text{gr. st.}}$$

- **Variational method:** Take $\psi_{\text{trial}} = \sum_n a_n |\psi_n\rangle$ where ψ_n is a trial wave function and the a_j 's are parameters of the wave function which we want to optimize to lower E_{trial} .

- Dirac's ket describes an abstract state of the particle (possibly position, possibly its Fourier transform, momentum).

- Back to the particle in a box:

- A possible trial wave function (that satisfies the boundary conditions) is

$$\psi_{\text{tr}} = (1+x)(1-x) = 1-x^2$$

¹We will prove that the approximate energy is an upper bound on the ground state energy in the homework.

- The energy of ψ_{tr} may be evaluated as follows.

$$\begin{aligned}
 E &= \frac{\int \psi_{\text{tr}}^*(x) \hat{H} \psi_{\text{tr}}(x) dx}{\int \psi_{\text{tr}}^*(x) \psi_{\text{tr}}(x) dx} \\
 &= \frac{\int_{-1}^1 (1-x^2) \left(-\frac{1}{2} \frac{d^2}{dx^2}\right) (1-x^2) dx}{\int_{-1}^1 (1-x^2)(1-x^2) dx} \\
 &= \frac{\int_{-1}^1 (1-x^2) dx}{\int_{-1}^1 (1-x^2)(1-x^2) dx} \\
 &= \frac{4/3}{16/15} \\
 &= \frac{5}{4} \\
 &= 1.25 \text{ a.u.}
 \end{aligned}$$

- From the exact solution to the particle in a box

$$E_1 = 1.23370055 < 1.25 = E_{\text{trial}}$$

so the variational theorem is satisfied.

- Next step: Trial wave function as a linear combination is $\psi_{\text{tr}}(x) = c_1 \psi_1(x) + c_2 \psi_2(x)$.
- Plugging this into the SE yields

$$c_1(\hat{H} - E)\psi_1(x) + c_2(\hat{H} - E)\psi_2(x) = 0$$

■ ψ_1, ψ_2 span the (Hilbert) space of solutions.

- To solve the above equation, multiply by $\psi_1^*(x)$ and integrate to obtain

$$c_1 \int_{-1}^1 \psi_1^*(x)(\hat{H} - E)\psi_1(x) dx + c_2 \int_{-1}^1 \psi_1^*(x)(\hat{H} - E)\psi_2(x) dx = 0$$

and multiply by $\psi_2^*(x)$ and integrate to obtain

$$c_1 \int_{-1}^1 \psi_2^*(x)(\hat{H} - E)\psi_1(x) dx + c_2 \int_{-1}^1 \psi_2^*(x)(\hat{H} - E)\psi_2(x) dx = 0$$

- Substituting, we have

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \quad c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0$$

- In matrix form, the above two equations become

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} - E \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\mathbb{H}\vec{c} - E\mathbb{S}\vec{c} = 0$$

- We get a matrix that has the same dimension as the size of the expansion (in the first case, we had a 1×1 matrix).
- \mathbb{S} is the overlap matrix because the wave functions aren't normalized.

5.2 Variational Method

- 10/27: • Approximating the ground state energy with some trial wave function and applying

$$E_{\text{approx}} = \frac{\int \psi_{\text{tr}}^* \hat{H} \psi_{\text{tr}} \, dx}{\int \psi_{\text{tr}}^* \psi_{\text{tr}} \, dx}$$

where

$$\psi_{\text{tr}} = \sum_n c_n \psi_n(x)$$

- Example 2:
- For our second term, we need another even function (since the ground state wavefunction is even). Thus, choose

$$\psi_{\text{tr}}(x) = c_1(1 - x^2) + c_2(1 - x^2)x^2$$

- Think about this in the context of power series — we have $(1 - x^2)$ times an even power series expansion $(c_1 + c_2x^2)$.
- To find c_1, c_2 , we could plug into the approximation integral and minimize.
- Alternatively, we can use matrices. We essentially project the Schrödinger equation onto the space of the two wave functions.
- Take $\hat{H}\psi = E\psi$ and expand it to $\hat{H}(c_1\psi_1 + c_2\psi_2) = E(c_1\psi_1 + c_2\psi_2)$. In matrix form, $\mathbb{H}\vec{c} = E\mathbb{S}\vec{c}$.
- We have an overlap matrix \mathbb{S} because our wave functions aren't normalized. If the basis *is* orthonormal, \mathbb{S} collapses to the identity matrix.
 - Each s_{ij} equals

$$s_{ij} = \int \psi_i^* \psi_j \, dx$$

- If ψ_1, ψ_2 is orthonormal, then $s_{ij} = \delta_{ij}$.
- The elements of the Hamiltonian matrix:

$$\begin{aligned} H_{11} &= \int \psi_1^*(x) \hat{H} \psi_1(x) \, dx \\ &= \frac{4}{3} \end{aligned}$$

$$\begin{aligned} H_{12} &= \int \psi_1^*(x) \hat{H} \psi_2(x) \, dx \\ &= \frac{8}{15} \end{aligned}$$

$$H_{21} = \frac{8}{15}$$

$$H_{22} = \frac{44}{105}$$

- Notice that \mathbb{H} is symmetric with $H_{12} = H_{21}$.
- Elements of the overlap matrix:

$$S_{11} = \frac{16}{15}$$

$$S_{12} = \frac{32}{105}$$

$$S_{21} = \frac{32}{105}$$

$$S_{22} = \frac{16}{315}$$

- Notice that \mathbb{S} is symmetric with $S_{12} = S_{21}$.
- Note that there are multiple ways to solve $\mathbb{H}\vec{c} = E\mathbb{S}\vec{c}$; McQuarrie and Simon (1997) only teaches one. Thus, you can get computers to do the math and solve far bigger systems than you could by hand.

- Solving $\mathbb{H}\vec{c} = E\mathbb{S}\vec{c}$ with the textbook method:
 - Rewrite as $(\mathbb{H} - E\mathbb{S})\vec{c} = 0$. Find the null space of $\mathbb{H} - E\mathbb{S}$.
 - Since the determinant is the product of the eigenvalues, $\det(\mathbb{H} - E\mathbb{S}) = (E_1 - E)(E_2 - E)$.
 - This determinant is equal to zero only when $E = E_1$ or $E = E_2$.
 - The energy is becoming quantized because of the linear algebra!
 - Now taking $\det(\mathbb{H} - E\mathbb{S})$ gives a characteristic polynomial in E .

$$\begin{aligned}
 0 &= \begin{vmatrix} \frac{4}{3} - \frac{16}{15}E & \frac{4}{15} - \frac{16}{105}E \\ \frac{4}{15} - \frac{16}{105}E & \frac{44}{105} - \frac{16}{315}E \end{vmatrix} \\
 &= \frac{256}{525} - \frac{2048}{4725}E + \frac{1024}{33075}E^2
 \end{aligned}$$

- Solving the quadratic gives us

$$E = 7 \pm \frac{\sqrt{133}}{2}$$

- Thus,

$$E_1 = 1.233\,718\,705 \text{ a.u.}$$

$$E_2 = 12.766 \text{ a.u.}$$

- Notice that the E_1 we found is only *marginally* greater than the real value of E_1 . Our value is accurate to four decimal places!
- Solving for \vec{c} with E_1 gives us

$$\vec{c}_1 = -0.9764$$

$$\vec{c}_2 = 0.2156$$

5.3 Perturbation Theory

10/29:

- Consider the Hamiltonian

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}$$

where \hat{H}_0 is the reference hamiltonian, \hat{V} is the perturbation, and λ is the perturbation parameter.

- The energy may be expressed as a Taylor series expansion in λ :

$$E(\lambda) = E(0) + \lambda \left. \frac{dE}{d\lambda} \right|_0 + \frac{\lambda^2}{2} \left. \frac{d^2E}{d\lambda^2} \right|_0 + \dots$$

- If λ is sufficiently small, we can get good approximations without resorting to higher order derivatives.
- It follows that our reference energy is

$$E(0) = \int \psi_0^* \hat{H}_0 \psi_0 \, dx$$

- We now have that

$$E(\lambda) = \int \psi^*(\lambda) \hat{H}(\lambda) \psi(\lambda) \, dx$$

- We also have from differentiating that

$$\frac{dE}{d\lambda} = \int \frac{d\psi}{d\lambda} \hat{H} \psi(\lambda) \, dx + \int \psi^*(\lambda) \hat{H}^* \frac{d\psi}{d\lambda} \, dx + \int \psi^* \frac{d\hat{H}}{d\lambda} \psi(\lambda) \, dx$$

$$\begin{aligned}
&= E \int \frac{d\psi^*}{d\lambda} \psi(\lambda) dx + E \int \psi^*(\lambda) \frac{d\psi}{d\lambda} dx + \int \psi^* \frac{d\hat{H}}{d\lambda} \psi(\lambda) dx \\
&= E \frac{d}{d\lambda} \left(\int \psi^*(\lambda) \psi(\lambda) dx \right) + \int \psi^* \hat{H} \psi dx \\
&= \int \psi^*(\lambda) \frac{d\hat{H}}{d\lambda} \psi(\lambda) dx \\
&= \int \psi^*(\lambda) \hat{V} \psi(\lambda) dx
\end{aligned}$$

– Note that the commutativity of \hat{H} follows from the fact that it's a Hermitian operator.

- It follows that

$$\left. \frac{dE}{d\lambda} \right|_{\lambda=0} = \int \psi_0^* V \psi_0 dx$$

- Richard Feynman worked this out for his undergraduate thesis at MIT. This laid the foundation of quantum electrodynamics, for which he would eventually win the Nobel prize.
- This is known as the **Hellmann-Feynman theorem** (1939).
- Note that the second derivative of $E(\lambda)$ unfortunately depends on $d\psi/d\lambda$.

- Many electron molecules: The Helium atom.

– We have $\hat{H}\psi = E\psi$ where

$$\hat{H} = -\frac{1}{2}\hat{\nabla}_1^2 - \frac{1}{2}\hat{\nabla}_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

- Note that the ∇ 's are Laplacians.
- This equation takes into account the kinetic and potential energy of two electrons, plus the electron-electron repulsion.
- Solve using perturbation theory. Our reference Hamiltonian is

$$\hat{H}_0 = \hat{H}_{\text{He}_1^+} + \hat{H}_{\text{He}_2^+} = \underbrace{-\frac{1}{2}\hat{\nabla}_1^2 - \frac{Z}{r_1}}_{\text{He}_1^+} + \underbrace{-\frac{1}{2}\hat{\nabla}_2^2 - \frac{Z}{r_2}}_{\text{He}_2^+}$$

- I.e., it's the sum of the Hamiltonians of two helium ions (one-electron systems like hydrogen).
- Since $\hat{V} = +1/r_{12}$, we have that

$$\hat{H}(1) = \hat{H}_0 + \hat{V}$$

is the Hamiltonian of the atom.

- Now we look for the solution to $\hat{H}_0\psi_0 + E_0\psi_0$.
- We know that

$$\psi_0 = \psi_{1s}(r_1\theta_1\phi_1)\psi_{1s}(r_2\theta_2\phi_2)$$

- The fact that only two electrons fit in an orbital emerges naturally from the quantum mechanics!
- We also know that

$$E_0 = -\frac{Z^2}{2n^2} - \frac{Z^2}{2n^2} = -4 \text{ a.u.}$$

- Thus, by perturbation theory,

$$\begin{aligned}
\left. \frac{dE}{d\lambda} \right|_{\lambda=0} &= \int \psi_0^* \hat{V} \psi_0 d\vec{r}_1 d\vec{r}_2 \\
&= \int 1s^*(1)1s^*(2) \hat{V} 1s(1)1s(2) d1 d2 \\
&= \frac{5}{8}Z
\end{aligned}$$

5.4 Chapter 7: Approximation Methods

From McQuarrie and Simon (1997).

- 11/2:
- Although the Schrödinger equation cannot be solved exactly for any system more complicated than the hydrogen atom, we can use either the **variational method** or **perturbation theory** to approximate solutions to Schrödinger equations to almost any desired accuracy.
 - We begin with the variational method.
 - If the ground-state wave function and corresponding energy of some arbitrary system are ψ_0 and E_0 , respectively, then

$$\begin{aligned}\hat{H}\psi_0 &= E_0\psi_0 \\ \psi_0^*\hat{H}\psi_0 &= \psi_0^*E_0\psi_0 \\ \int \psi_0^*\hat{H}\psi_0 d\tau &= E_0 \int \psi_0^*\psi_0 d\tau \\ E_0 &= \frac{\int \psi_0^*\hat{H}\psi_0 d\tau}{\int \psi_0^*\psi_0 d\tau}\end{aligned}$$

where $d\tau$ represents the appropriate volume element for integrating over all space.

- **Variational principle:** If ϕ is any function, then

$$\frac{\int \phi^*\hat{H}\phi d\tau}{\int \phi^*\phi d\tau} = E_\phi \geq E_0 = \frac{\int \psi_0^*\hat{H}\psi_0 d\tau}{\int \psi_0^*\psi_0 d\tau}$$

and $E_\phi = E_0$ iff $\phi = \psi_0$ ^[2].

- Essentially, the variational method consists of choosing a trial function ϕ that depends on **variational parameters** (numbers) so that E_ϕ depends on the variational parameters, too, and minimizing E_ϕ over the parameters.
- McQuarrie and Simon (1997) does a worked example with the ground state of the hydrogen atom, comparing answers with the exact solution.
 - Uses the formula for E_ϕ to directly express it in terms of the variational parameter and then differentiates to find the maxima.
 - Applied to a case that can be solved exactly, the variational method with a trial wave function of the appropriate form will give the exact solution.
- Estimating the ground state energy of a helium atom, and deriving effective nuclear charge.
 - Consider the Hamiltonian for helium from the end of Chapter 6.
 - It can be written in the form

$$\hat{H} = \hat{H}_H(1) + \hat{H}_H(2) + \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}}$$

where $\hat{H}_H(j)$, $j = 1, 2$, is the Hamiltonian operator for a single electron around a helium nucleus.

- Ignoring the interelectron repulsion term gives us a separable wave function of the form

$$\phi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)$$

- We use the above as our trial wave function with Z (see Table 4.6) as our variational parameter.

²See Problem ?? for a proof of the variational principle.

- Minimizing gives us $Z_{\min} = 27/16$ and a fairly good E_{\min} value.
- Note that Z_{\min} can naturally be interpreted as the **effective nuclear charge**.
- Since $Z_{\min} < 2$, we have that each electron partially **screens** the nucleus from the other.
- McQuarrie and Simon (1997) arrives at the two linear algebraic equations Mazziotti did by expanding $\int \phi \hat{H} \phi d\tau$ with $\phi = c_1 f_1 + c_2 f_2$, applying the condition that H is Hermitian from Chapter 4 to show that $H_{ij} = H_{ji}$ and $S_{ij} = S_{ji}$, and differentiating the resulting energy function with respect to c_1 and then with respect to c_2 .
- **Matrix elements:** The quantities H_{ij} and S_{ij} .
- **Secular determinant:** A determinant of the form

$$\begin{vmatrix} H_{11} - ES_{11} & \cdots & H_{1n} - ES_{1n} \\ \vdots & & \vdots \\ H_{n1} - ES_{n1} & \cdots & H_{nn} - ES_{nn} \end{vmatrix}$$

- There exists a solution to the linear algebraic equations iff the secular determinant vanishes (equals 0).
- **Secular equation:** The equation obtained by expanding the secular determinant.
 - The smaller root of a second-degree secular equation is an upper bound on the ground state energy.
 - The larger root of a second-degree secular equation is an upper bound on the energy of the first excited state (albeit usually a crude one; we do not investigate methods of approximating energies other than that of the ground state here).
- Normalizing the trial wave function.
 - Since the linear system is homogenous, all of the c_1 terms (for example) can be expressed as a linear combination of all of the other terms.
 - From here, we can find the ratios $c_2/c_1, c_3/c_1, \dots, c_N/c_1$.
 - Thus, we simply integrate the modulus squared of our trial wave function with c_1 free and set the result equal to 1. Solving for c_1 normalizes the equation.
- Note that trial wave functions can be linear combinations of functions that also contain variational parameters, but minimization here must be done numerically as the system is no longer linear.
- We now discuss perturbation theory.
- Suppose we cannot solve the Schrödinger equation $\hat{H}\psi = E\psi$ but we can solve $\hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$, which corresponds to a system that is in some sense similar to the unsolvable system. Then let $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$.
- **Unperturbed Hamiltonian operator:** The Hamiltonian operator corresponding to the system we can solve exactly. Denoted by $\hat{H}^{(0)}$.
- **Perturbation:** The difference between the Hamiltonian operator we cannot solve and the unperturbed Hamiltonian operator. Denoted by $\hat{H}^{(1)}$.
- In perturbation theory, we let

$$\psi = \psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \dots \qquad E = E^{(0)} + E^{(1)} + E^{(2)} + \dots$$

where $\psi^{(1)}, \psi^{(2)}, \dots$ and $E^{(1)}, E^{(2)}, \dots$ are successive corrections to $\psi^{(0)}$ and $E^{(0)}$, respectively.

- We can show (see Problem ??) that

$$E^{(1)} = \int \psi^{(0)*} \hat{H}^{(1)} \psi^{(0)} d\tau$$

- Note that we can (although we will not here) derive explicit expressions for higher order corrections. These do get messy though.
- Uses perturbation theory to derive the energy of a particle in a one-dimensional slanted box, and separately the energy of a Helium electron.