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 $L = 2\,\text{a.u.}$ 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
    $$H\psi(x) = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x)$$
    or, in atomic units,
    $$H\psi(x) = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x)$$
- **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
    $$\psi_{\text{tr}} = (1+x)(1-x) = 1 - x^2$$

[1]We 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.

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

- 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

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

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

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

- Substituting, we have

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

- 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 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

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

  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

$$s_{ij} = \int \psi_i^* \psi_j \, \mathrm{d}x$$

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

$$\begin{aligned} H_{11} &= \int \psi_1^*(x) \hat{H} \psi_1(x) \, \mathrm{d}x \\ &= \frac{4}{3} \end{aligned} \qquad \begin{aligned} H_{12} &= \int \psi_1^*(x) \hat{H} \psi_2(x) \, \mathrm{d}x \\ &= \frac{8}{15} \end{aligned}$$

$$H_{21} = \frac{8}{15} \qquad H_{22} = \frac{44}{105}$$

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

$$S_{11} = \frac{16}{15} \qquad S_{12} = \frac{32}{105}$$

$$S_{21} = \frac{32}{105} \qquad S_{22} = \frac{16}{315}$$

  - 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,

$$E_1 = 1.233\,718\,705\,\text{a.u.} \qquad E_2 = 12.766\,\text{a.u.}$$

    - 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

$$\vec{c}_1 = -0.9764 \qquad \vec{c}_2 = 0.2156$$

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:

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

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

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

- We now have that

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

- We also have from differentiating that

$$\frac{\mathrm{d}E}{\mathrm{d}\lambda} = \int \frac{\mathrm{d}\psi}{\mathrm{d}\lambda}\hat{H}\psi(\lambda)\,\mathrm{d}x + \int \psi^*(\lambda)\hat{H}^*\frac{\mathrm{d}\psi}{\mathrm{d}\lambda}\,\mathrm{d}x + \int \psi^*\frac{\mathrm{d}\hat{H}}{\mathrm{d}\lambda}\psi(\lambda)\,\mathrm{d}x$$

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

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

- It follows that
$$\left.\frac{\mathrm{d}E}{\mathrm{d}\lambda}\right|_{\lambda=0} = \int \psi_0^* V\psi_0\,\mathrm{d}x$$
  - 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 $\mathrm{d}\psi/\mathrm{d}\lambda$.
- 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
$$\hat{H}_0 = \hat{H}_{\mathrm{He}_1^+} + \hat{H}_{\mathrm{He}_2^+} = \underbrace{-\frac{1}{2}\hat{\nabla}_1^2 - \frac{Z}{r_1}}_{\mathrm{He}_1^+}\underbrace{-\frac{1}{2}\hat{\nabla}_2^2 - \frac{Z}{r_2}}_{\mathrm{He}_2^+}$$
    - 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
$$\psi_0 = \psi_{1s}(r_1\theta_1\phi_1)\psi_{1s}(r_2\theta_2\psi_2)$$
    - 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,
$$\begin{aligned}
\left.\frac{\mathrm{d}E}{\mathrm{d}\lambda}\right|_{\lambda=0} &= \int \psi_0^*\hat{V}\psi_0\,\mathrm{d}\vec{r}_1\,\mathrm{d}\vec{r}_2 \\
&= \int 1\mathrm{s}^*(1)1\mathrm{s}^*(2)\hat{V}1\mathrm{s}(1)1\mathrm{s}(2)\,\mathrm{d}1\,\mathrm{d}2 \\
&= \frac{5}{8}Z
\end{aligned}$$