

## 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<sup>[1]</sup>,

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

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

- 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

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

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

- The energy of  $\psi_{\text{tr}}$  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

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

■  $\psi_1, \psi_2$  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 the same dimension as the size of the expansion (in the first case, we had a  $1 \times 1$  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  $\psi_1, \psi_2$  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  $\lambda$  is the perturbation parameter.

- The energy may be expressed as a Taylor series expansion in  $\lambda$ :

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

- If  $\lambda$  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  $\nabla$ '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  $\psi_0$  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  $\phi$  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  $\phi = \psi_0$ <sup>[2]</sup>.

- Essentially, the variational method consists of choosing a trial function  $\phi$  that depends on **variational parameters** (numbers) so that  $E_\phi$  depends on the variational parameters, too, and minimizing  $E_\phi$  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  $E_\phi$  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.

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<sup>2</sup>See 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.