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 $\psi_{\text{trial}} = \sum_n a_n \left|\psi_n\right\rangle$ 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.