PH 422: Quantum Mechanics II
Tutorial Sheet 3

This tutorial sheet contains problems related to the use of variational principle in quantum mechanics.

1. Obtain the energy of the ground state of a one-dimensional (1D) simple-harmonic oscillator (SHO) using the trial wave function $\psi(x) = ce^{-\alpha x^2}$, where c is the normalization constant, and α is the variational parameter.
   Soln: Let us estimate the ground state of one-dimensional simple harmonic oscillator using the trial wave function of the form $\psi(x) = ce^{-\alpha x^2}$ Because this function is of the form exact wave function, the obtained energy should be exact ground state energy $\frac{\hbar\omega}{2}$. Let us first normalize $\psi(x)$

$$\langle\psi|\psi\rangle = c^2 \int_{-\infty}^{\infty} e^{-2\alpha x^2} dx = 1$$

Substitute $t = \sqrt{2\alpha}x$

$$\Rightarrow \langle\psi|\psi\rangle = \frac{c^2}{\sqrt{2\alpha}} \int_{-\infty}^{\infty} e^{-t^2} dt = c^2\sqrt{\frac{\pi}{2\alpha}} = 1$$
$$\Rightarrow c = \left(\frac{2\alpha}{\pi}\right)^{1/4}$$

Above we used value of the Gaussian integral $\int_{-\infty}^{\infty} e^{-t^2} dt = \sqrt{\pi}$.Now

$$E(\alpha) = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \sqrt{\frac{2\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-\alpha x^2}\Big(- \frac{\hbar^2}{2m}\frac{d^2}{dx^2} e^{-\alpha x^2} + \frac{1}{2} m\omega^2 x^2 e^{-\alpha x^2}\Big) dx$$

Now

$$\frac{d^2}{dx^2}\big\{e^{-\alpha x^2}\big\} = \frac{d}{dx}\big(- 2\alpha x e^{-\alpha x^2}\big)$$
$$= \Bigg(- 2\alpha e^{-\alpha x^2} + 4\alpha^2 x^2 e^{-\alpha x^2}\Bigg)$$

$$\Rightarrow E(\alpha) = \sqrt{\frac{2\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-\alpha x^2}\Big(- \frac{\hbar^2}{2m}\frac{d^2}{dx^2} e^{-\alpha x^2} + \frac{1}{2} m\omega^2 x^2 e^{-\alpha x^2}\Big) dx$$

Using the standard integral

$$\int_{-\infty}^{\infty} x^{2n} e^{-\frac{x^2}{a^2}} dx = \sqrt{\pi}\frac{a^{2n+1}(2n-1)!}{2^n}$$

We have

$$\int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx = \frac{\sqrt{\pi}}{2}\Big(\frac{1}{\sqrt{2\alpha}}\Big)^3$$

So that

$$E(\alpha) = \left\{ \sqrt{\frac{2\alpha}{\pi}} 2\alpha \sqrt{\frac{\pi}{2\alpha}} \frac{\hbar^2}{2m} - \frac{\hbar^2}{2m} \sqrt{\frac{2\alpha}{\pi}} 4\alpha^2 \frac{\sqrt{\pi}}{2} \frac{1}{(2\alpha)^{3/2}} + \frac{1}{2} m\omega^2 \frac{\sqrt{\pi}}{2\sqrt{\pi}} \frac{\sqrt{2\alpha}}{(2\alpha)^{3/2}} \right\}$$

$$E(\alpha) = \left\{ \frac{\hbar^2}{2m}\alpha + \frac{m\omega^2}{8\alpha} \right\}$$

$$\frac{dE}{d\alpha} = 0 \Rightarrow \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} = 0$$
$$\Rightarrow \alpha = \frac{m\omega}{2\hbar}$$

$$\Rightarrow E_{min} = \frac{\hbar^2}{2m}\frac{m\omega}{2\hbar} + \frac{m\omega^2}{8} \times \frac{m\omega}{2\hbar}$$
$$\Rightarrow \boxed{\begin{aligned} E_{min} &= \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} = \frac{\hbar\omega}{2} \\ &= E_0 (\text{Exact GS}) \end{aligned}}$$

and

$$\boxed{\begin{aligned} \psi(x) &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}} \\ &= \psi_0(x) \end{aligned}}$$

Thus, as expected, we recover the exact ground state energy and wave function for this trial wave function

2. In the variational principle as applied to quantum mechanics, one minimizes the integral $I = \langle\psi|H|\psi\rangle = \int\{-\frac{\hbar^2}{2m}\psi^*\nabla^2\psi + V\psi^*\psi\}d^3\mathbf{r}$, subject to the normalization condition $\int \psi^*\psi d^3\mathbf{r} = 1$. Show using integration by parts, that one can also use the expression $I = \int\{\frac{\hbar^2}{2m}\nabla\psi^* \cdot \nabla\psi + V\psi^*\psi\}d^3\mathbf{r}$.
   Soln:

$$I = \int \left\{ -\frac{\hbar^2}{2m}\psi^*\nabla^2\psi + V\psi^*\psi \right\} d^3\mathbf{r}$$

The second term remains unchanged so we concentrate only on the first term

$$\begin{aligned} I_1 &= -\frac{\hbar^2}{2m}\int \psi^*\nabla^2\psi d^3\mathbf{r} \\ &= -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^* \left\{ \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} \right\} dxdydz \end{aligned} \tag{1}$$

Let us consider the first integral and apply integration by parts

$$\begin{aligned} I_{1x} &= -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^*\frac{\partial^2\psi}{\partial x^2} dxdydz \\ &= -\frac{\hbar^2}{2m}\left\{ \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \psi^* \frac{\partial\psi}{\partial x}\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\partial\psi^*}{\partial x}\frac{\partial\psi}{\partial x} dxdydz \right\} \end{aligned}$$

the first term on the RHS vanishes because $\psi^*(x = \pm\infty, y, z) = 0$, because wave function (and its complex conjugate) must vanish at infinity for it to be normalizable

$$I_{1x} = \frac{\hbar^2}{2m}\int\int\int \frac{\partial \psi^*}{\partial x}\frac{\partial \psi}{\partial x} dxdydz \tag{2}$$

Similarly we can show

$$\begin{aligned} I_{1y} &= -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^* \frac{\partial^2 \psi}{\partial y^2} dxdydz \\ &= \frac{\hbar^2}{2m}\int\int\int \frac{\partial \psi^*}{\partial y}\frac{\partial \psi}{\partial y} dxdydz \end{aligned} \tag{3}$$

and

$$\begin{aligned} I_{1z} &= -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^* \frac{\partial^2 \psi}{\partial z^2} dxdydz \\ &= \frac{\hbar^2}{2m}\int\int\int \frac{\partial \psi^*}{\partial z}\frac{\partial \psi}{\partial z} dxdydz \end{aligned} \tag{4}$$

using Eq.(2),Eq.(3),Eq.(4) in Eq.(1), we have

$$I_1 = \frac{\hbar^2}{2m}\int \left\{ \frac{\partial \psi^*}{\partial x}\frac{\partial \psi}{\partial x} + \frac{\partial \psi^*}{\partial y}\frac{\partial \psi}{\partial y} + \frac{\partial \psi^*}{\partial z}\frac{\partial \psi}{\partial z} \right\} d^3\mathbf{r}$$

but

$$\begin{aligned} \frac{\partial \psi^*}{\partial x}\frac{\partial \psi}{\partial x} + \frac{\partial \psi^*}{\partial y}\frac{\partial \psi}{\partial y} + \frac{\partial \psi^*}{\partial z}\frac{\partial \psi}{\partial z} &= \left(\hat{i}\frac{\partial \psi^*}{\partial x} + \hat{j}\frac{\partial \psi^*}{\partial y} + \hat{k}\frac{\partial \psi^*}{\partial z}\right).\left(\hat{i}\frac{\partial \psi}{\partial x} + \hat{j}\frac{\partial \psi}{\partial y} + \hat{k}\frac{\partial \psi}{\partial z}\right) \\ &= (\vec{\nabla}\psi^*).\vec{\nabla}\psi \end{aligned}$$

$$\Rightarrow I_1 = \frac{\hbar^2}{2m}\int (\vec{\nabla}\psi^*)\cdot(\vec{\nabla}\psi) d^3\mathbf{r}$$

3. Estimate the ground state energy of a 1D-SHO using the trial wave function of the form $\psi(x) = Ce^{-\alpha|x|}$, treating α as a variational parameter. (Helpful integral: $\int_0^\infty e^{-\alpha x} x^n dx = \frac{n!}{\alpha^{n+1}}$.)

Soln: First we normalise $\psi(x)$

$$c^2\int_{-\infty}^{\infty} e^{-2\alpha|x|}dx$$

$$\begin{aligned} \Rightarrow c^2\int_{-\infty}^{0} e^{2\alpha x} + c^2\int_{0}^{\infty} e^{-2\alpha x}dx = 1 \\ \Rightarrow \frac{c^2}{2\alpha} + \frac{c^2}{2\alpha} = 1 \\ \Rightarrow c = \sqrt{\alpha} \end{aligned}$$

$$\boxed{\psi(x) = \sqrt{\alpha}e^{-\alpha|x|}}$$

Because the slope of this wave function is discontinuous at $x = 0$, so $\frac{\partial^2\psi}{\partial x^2}$ is not defined there. Therefore, we use expression of Prob. 2 for computing energy expectation value

$$\begin{aligned}
E(\alpha) &= \langle\psi(\alpha)|H|\psi(\alpha)\rangle \\
&= \int_{-\infty}^{\infty}\left\{\frac{\hbar^2}{2m}\left(\frac{d\psi}{dx}\right)^2 + V\psi^2\right\}dx \\
&= \frac{\hbar^2\alpha}{2m}\int_{-\infty}^{0}\left(\frac{de^{\alpha x}}{dx}\right)^2 dx + \frac{\hbar^2\alpha}{2m}\int_{0}^{\infty}\left(\frac{de^{-\alpha x}}{dx}\right)^2 dx + \frac{1}{2}m\omega^2\alpha\int_{-\infty}^{0} x^2e^{2\alpha x}dx + \frac{1}{2}m\omega^2\alpha\int_{0}^{\infty} x^2e^{-2\alpha x}dx
\end{aligned}$$

using

$$\begin{aligned}
\int_{-\infty}^{0} x^2e^{2\alpha x}dx = \int_{0}^{\infty} x^2e^{-2\alpha x}dx &= \frac{2!}{(2\alpha)^3} \\
&= \frac{1}{4\alpha^3}
\end{aligned}$$

$$\begin{aligned}
E(\alpha) &= \frac{\hbar^2\alpha^3}{2m}\int_{-\infty}^{0} e^{2\alpha x}dx + \frac{\hbar^2\alpha^3}{2m}\int_{0}^{\infty} e^{-2\alpha x}dx + \frac{m\omega^2}{4\alpha^2} \\
&= \frac{\hbar^2\alpha^3}{4m\alpha} + \frac{\hbar^2\alpha^3}{4m\alpha} + \frac{m\omega^2}{4\alpha^2}
\end{aligned}$$

$$\boxed{E(\alpha) = \frac{\hbar^2\alpha^2}{2m} + \frac{m\omega^2}{4\alpha^2}} \tag{5}$$

$$\frac{dE}{d\alpha} = 0 \Rightarrow \frac{\hbar^2\alpha}{m} - \frac{m\omega^2}{2\alpha^3} = 0$$

$$\begin{aligned}
&\Rightarrow \alpha^4 = \frac{m^2\omega^2}{2\hbar^2} \\
&\Rightarrow \alpha = \pm\frac{1}{2^{1/4}}\sqrt{\frac{m\omega}{\hbar}}
\end{aligned} \tag{6}$$

but only $\alpha = \frac{1}{2^{1/4}}\sqrt{\frac{m\omega}{\hbar}}$ will lead to a normalizable wave function, using this in Eq.(5), we have

$$E_{min} = \frac{\hbar^2}{2m} \times \frac{m\omega}{\hbar\sqrt{2}} + \frac{m\omega^2}{4} \times \frac{\sqrt{2}\hbar}{m\omega}$$

$$\boxed{E_{min} = \frac{1}{\sqrt{2}}\hbar\omega > \frac{1}{2}\hbar\omega}$$

4. Show that for a 1D-SHO, if one uses a trial wave function $\psi(x) = cxe^{-\alpha x^2}$,where c is the normalization constant and α is the variational parameter, one obtains exact

energy $E = \frac{3}{2}\hbar\omega$ of the first excited state.

Soln: Let us first normalize the trial wave function

$$c^2 \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx$$

using the result

$$\int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx = \frac{\sqrt{\pi}}{2}\Big(\frac{1}{\sqrt{2\alpha}}\Big)^3$$

we have above

$$\int_{-\infty}^{\infty} \psi^2(x) dx = \frac{c^2}{2}\sqrt{\frac{\pi}{8\alpha^3}} = 1$$

$$\Rightarrow c^2 = 4\sqrt{2}\sqrt{\frac{\alpha^3}{\pi}}$$

$$\Rightarrow c = 2\bigg(\frac{2\alpha^3}{\pi}\bigg)^{\frac{1}{4}}$$

$$\Rightarrow \psi(x) = 2\bigg(\frac{2\alpha^3}{\pi}\bigg)^{\frac{1}{4}} x e^{-\alpha x^2}$$

$$\Rightarrow \frac{d\psi(x)}{dx} = 2\bigg(\frac{2\alpha^3}{\pi}\bigg)^{\frac{1}{4}} e^{-\alpha x^2} - 4\bigg(\frac{2\alpha^3}{\pi}\bigg)^{\frac{1}{4}} \alpha x^2 e^{-\alpha x^2}$$

$$\Rightarrow \bigg(\frac{d\psi}{dx}\bigg)^2 = 4\bigg(\frac{2\alpha^3}{\pi}\bigg)^{\frac{1}{2}} e^{-2\alpha x^2} + 16\bigg(\frac{2\alpha^3}{\pi}\bigg)^{\frac{1}{2}} \alpha^2 x^4 e^{-2\alpha x^2} - 16\bigg(\frac{2\alpha^3}{\pi}\bigg)^{\frac{1}{2}} \alpha x^2 e^{-2\alpha x^2}$$

We will use the expression of problem 2 to compute the energy expectation value

$$\begin{aligned} E(\alpha) &= \langle\psi(\alpha)|H|\psi(\alpha)\rangle \\ &= \frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\left(\frac{d\psi}{dx}\right)^2 dx + \frac{1}{2}m\omega^2\int_{-\infty}^{\infty} x^2\psi^2(x)dx \\ &= \frac{\hbar^2}{2m}\times 4\left(\frac{2\alpha^3}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} e^{-2\alpha x^2}dx + \frac{\hbar^2}{2m}16\alpha^2\left(\frac{2\alpha^3}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x^4 e^{-2\alpha x^2}dx \\ &\quad - \frac{\hbar^2}{2m}16\alpha\left(\frac{2\alpha^3}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2}dx + \frac{1}{2}m\omega^2\times 4\left(\frac{2\alpha^3}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x^4 e^{-2\alpha x^2}dx \end{aligned}$$

using the integrals

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

and

$$\int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} = \frac{3!!}{2^2\alpha^2}\sqrt{\frac{\pi}{\alpha}} = \frac{3}{4\alpha^2}\sqrt{\frac{\pi}{\alpha}}$$

we have

$$
\begin{aligned}
E(\alpha) &= \frac{2\hbar^2}{m}\left(\frac{2\alpha^3}{\pi}\right)^{1/2}\sqrt{\frac{\pi}{\alpha}} + \frac{8\hbar^2}{m}\left(\frac{2\alpha^3}{\pi}\right)^{1/2}\alpha^2\frac{3}{4(2\alpha)^2}\sqrt{\frac{\pi}{2\alpha}} - \frac{8\hbar^2}{m}\left(\frac{2\alpha^3}{\pi}\right)^{1/2}\alpha\frac{1}{2}\sqrt{\frac{\pi}{8\alpha^3}} \\
&\qquad + 2\omega^2 m\left(\frac{2\alpha^3}{\pi}\right)^{1/2}\alpha^2\frac{3}{4(2\alpha)^2}\sqrt{\frac{\pi}{2\alpha}} \\
&= \frac{2\hbar^2\alpha}{m} + \frac{8\hbar^2 \times 3\alpha \times \alpha^2}{m \times 4 \times 4\alpha^2} - \frac{8\hbar^2\alpha}{4m} + \frac{2m\omega^2 \times 3\alpha}{16\alpha^2} \\
&= \frac{3\hbar^2\alpha}{2m} + \frac{3m\omega^2}{8\alpha}
\end{aligned}
$$

$$
\begin{aligned}
E(\alpha) &= \frac{3\hbar^2\alpha}{2m} + \frac{3m\omega^2}{8\alpha} \\
\frac{dE}{d\alpha} = 0 &\Rightarrow \frac{3\hbar^2}{2m} - \frac{3m\omega^2}{8\alpha^2} = 0
\end{aligned}
$$

$$
\begin{aligned}
&\Rightarrow \alpha^2 = \frac{m^2\omega^2}{4\hbar^2} \\
&\Rightarrow \alpha = \frac{m\omega}{2\hbar}
\end{aligned}
$$

$$
E_{min} = E(\alpha = \frac{m\omega}{2\hbar}) = \frac{3}{4}\hbar\omega + \frac{3}{4}\hbar\omega
$$

$$
\boxed{E_{min} = \frac{3}{2}\hbar\omega}
$$

which is exact result

5. Here we derive the "linear-combination of basis functions approach", quite commonly used in quantum mechanics, using a variational principle. Suppose that the Hamiltonian of a system is given by H, and we assume that the state ket $|\psi\rangle$ corresponding to its ground state can be approximated as

$$
|\psi\rangle = \sum_{j=1}^{N} C_j |j\rangle,
$$

where $|j\rangle$ denote the known basis kets, while C_j are the unknown expansion coefficients which are also the variational parameters in this approach, and, in general, are complex. In the $\mathbf{r}$ representation, the following notation is adopted $\psi(\mathbf{r}) = \langle \mathbf{r}|\psi\rangle$, and $\phi_j(\mathbf{r}) = \langle \mathbf{r}|j\rangle$. Using the variational principle, show that the ground state energy E, and the state ket $|\psi\rangle$ can be obtained by solving the generalized eigenvalue problem

$$
\tilde{H}\tilde{C} = E\tilde{S}\tilde{C},
$$

where $\tilde{H}$ and $\tilde{S}$ denote the $N \times N$ matrices, representing the Hamiltonian and the overlap, with elements defined as $H_{ij} = \langle i|H|j\rangle$, $S_{ij} = \langle i|j\rangle$, respectively, while C_i form the N elements of the column vector $\tilde{C}$, denoting the ground state eigenfunction. Note that form an orthonormal basis set, $\langle i|j\rangle = \delta_{ij}$ so that $\tilde{S} = I$, and the previous generalized eigenvalue problem reduces to a normal eigenvalue problem.
Soln: According to the variational principle, we should minimize

$$E(C_i, C_i^*) = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle},$$

with respect to the variational coefficients C_i, $i = 1, 2, 3, \ldots N$. Using the given expansion of $|\psi\rangle$, and the definitions of $\tilde{H}_{ij} = \langle i|H|j\rangle$ and $\tilde{S}_{ij} = \langle i|j\rangle$,we obtain

$$E(C_i, C_i^*) = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_{j,k} C_k^* C_j \langle k|H|j\rangle}{\sum_{j,k} C_k^* C_j \langle k|j\rangle} = \frac{\sum_{j,k} C_k^* C_j H_{kj}}{\sum_{j,k} C_k^* C_j S_{kj}}. \tag{7}$$

The variational principle in the present case implies that the conditions

$$\left.\begin{aligned} \frac{\partial E}{\partial C_i} &= 0 \\ \frac{\partial E}{\partial C_i^*} &= 0 \end{aligned}\right. \quad \text{for } i = 1, 2, 3, \ldots N \tag{8}$$

must hold. Because C_i's are complex, therefore, C_i and C_i^* are independent variables. Using the results $\frac{\partial C_i}{\partial C_j} = \frac{\partial C_i^*}{\partial C_j^*} = \delta_{ij}$ and $\frac{\partial C_i^*}{\partial C_j} = \frac{\partial C_i}{\partial C_j^*} = 0$, we obtain on applying Eq. 8 on Eq. 7

$$\frac{\partial E}{\partial C_i} = \frac{(\sum_{j,k} C_k^* \delta_{ij} \tilde{H}_{kj})(\sum_{j,k} C_k^* C_j S_{kj}) - (\sum_{j,k} C_k^* C_j H_{kj})(\sum_{j,k} C_k^* \delta_{ij} S_{kj})}{(\sum_{j,k} C_k^* C_j S_{kj})^2} = 0.$$

This can be written as

$$\begin{aligned} \frac{\partial E}{\partial C_i} &= \frac{(\sum_k C_k^* H_{ki}) - \left(\frac{\sum_{j,k} C_k^* C_j H_{kj}}{\sum_{j,k} C_k^* C_j S_{kj}}\right)(\sum_k C_k^* S_{ki})}{(\sum_{j,k} C_k^* C_j S_{kj})} = 0 \\ \Longrightarrow (\sum_k C_k^* H_{ki}) &- \left(\frac{\sum_{j,k} C_k^* C_j H_{kj}}{\sum_{j,k} C_k^* C_j S_{kj}}\right)(\sum_k C_k^* S_{ki}) = 0. \end{aligned}$$

Now, on using Eq. 7 in the second term above, we have

$$(\sum_k C_k^* H_{ki}) - E(\sum_k C_k^* S_{ki}) = 0. \tag{9}$$

The complex conjugate of the previous equation yields

$$(\sum_k C_k H_{ki}^*) - E(\sum_k C_k S_{ki}^*) = 0.$$

Using the fact that $\tilde{H}$ and $\tilde{S}$ are Hermitian matrices, we have $H_{ki}^* = H_{ik}$ and $S_{ki}^* = S_{ik}$. On substituting these in previous equation, we obtain

$$\sum_k H_{ik} C_k = E \sum_k S_{ki} C_k$$
$$\implies \tilde{H}\tilde{C} = E\tilde{S}\tilde{C}. \tag{10}$$

This equation is called a generalized eigenvalue problem because of the presence of the overlap matrix $\tilde{S}$ on the RHS, and clearly reduces to the normal eigenvalue problem $\tilde{H}\tilde{C} = E\tilde{C}$, for an orthonormal basis ($\tilde{S} = I$). Note that we obtained this equation by taking the complex conjugate of the original equation 9, which actually is an eigenvalue problem for the complex conjugates of the coefficients, C_k^* or $\tilde{C}^\dagger$ (i.e., for $\langle\psi|$). You can verify that if we start with the condition $\frac{\partial E}{\partial C_i^*} = 0$, we will directly get the eigenvalue problem of Eq. 10.

6. This problem is a simple application of the linear-combination of basis functions approach. Suppose the wave function of a given quantum mechanical system can be expanded in terms of three basis functions $\{|i\rangle, i = 1, 2, 3\}$, which form an orthonormal set $\langle i|j\rangle = \delta_{ij}$. Defining the Hamiltonian matrix elements with respect to these basis functions as $H_{ij} = \langle i|H|j\rangle$, it is given that the only non-zero Hamiltonian matrix elements are $H_{12} = H_{21} = H_{23} = H_{32} = H_{13} = H_{31} = t$, where t is a real positive number. Obtain the eigenvalues and eigenvectors of this Hamiltonian. How do the results change when we set $H_{13} = H_{31} = 0$?
Soln:

(a) With

$$H = \begin{pmatrix} 0 & t & t \\ t & 0 & t \\ t & t & 0 \end{pmatrix}$$

the characteristic polynomial is

$$\begin{vmatrix} -\lambda & t & t \\ t & -\lambda & t \\ t & t & -\lambda \end{vmatrix} = 0$$

$$\begin{aligned}
&\Rightarrow -\lambda\left(\lambda^2 - t^2\right) + t\left(t^2 + t\lambda\right) + t\left(t^2 + t\lambda\right) = 0 \\
&\Rightarrow 2t^2(t+\lambda) - \lambda(\lambda - t)(\lambda + t) = 0 \\
&\Rightarrow (\lambda + t)\left(2t^2 - \lambda^2 + \lambda t\right) = 0 \\
&\Rightarrow \lambda = -t
\end{aligned}$$

or

$$\begin{aligned}
&\Rightarrow \lambda^2 - \lambda t - 2t^2 = 0 \\
&\Rightarrow \lambda^2 - 2\lambda t + \lambda t - 2t^2 = 0 \\
&\Rightarrow \lambda(\lambda - 2t) + t(\lambda - 2t) = 0 \\
&\Rightarrow (\lambda + t)(\lambda - 2t) = 0 \\
&\Rightarrow \lambda = -t, \lambda = 2t
\end{aligned}$$

$$\Rightarrow \lambda = -t \qquad \text{degenerate}$$
$$\lambda = 2t$$

Let's find the eigenvectors

(i) $\lambda = -t$

$$(H - \lambda I)c = 0$$
$$\Rightarrow \begin{pmatrix} t & t & t \\ t & t & t \\ t & t & t \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0$$
$$\Rightarrow \quad c_1 + c_2 + c_3 = 0$$

Two possibilities

$$|\lambda = -t\rangle_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$$

$$|\lambda = -t\rangle_2 = \frac{1}{\sqrt{6}} \begin{pmatrix} 1 \\ -2 \\ 1 \end{pmatrix}$$

(ii) $\lambda = 2t$

$$(H - \lambda I)c = 0$$
$$\Rightarrow \begin{pmatrix} -2t & t & t \\ t & -2t & t \\ t & t & -2t \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0$$
$$\Rightarrow \quad -2c_1 + c_2 + c_3 = 0$$
$$c_1 - 2c_2 + c_3 = 0$$
$$c_1 + c_2 - 2c_3 = 0$$

Any two of these equations are linearly independent. A possible solution which orthogonal to $|\lambda\rangle_1$ and $|\lambda\rangle_2$is

$$|\lambda = 2t\rangle_3 = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$$

(b) When $H_{13} = H_{31} = 0$, we have

$$H = \begin{pmatrix} 0 & t & 0 \\ t & 0 & t \\ 0 & t & 0 \end{pmatrix}$$

$|H - \lambda I| = 0$ is

$$\begin{vmatrix} -\lambda & t & 0 \\ t & -\lambda & t \\ 0 & t & -\lambda \end{vmatrix} = 0$$

$$
\begin{aligned}
&\Rightarrow -\lambda\left(\lambda^2 - t^2\right) + t^2\lambda = 0 \\
&\Rightarrow \lambda(\lambda^2 - 2t^2) = 0 \\
&\Rightarrow \lambda = 0, \pm t\sqrt{2}
\end{aligned}
$$

Let's find the eigenvectors

(i) $\lambda = 0$

$$
\begin{aligned}
& (H - \lambda I)c = 0 \\
\Rightarrow \quad & \begin{pmatrix} 0 & t & 0 \\ t & 0 & t \\ 0 & t & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0 \\
\Rightarrow \quad & c_2 = 0 \\
& c_1 + c_3 = 0 \\
& |\lambda = 0\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}
\end{aligned}
$$

(ii) $\lambda = \pm\sqrt{2}t$

$$
\begin{aligned}
& (H - \lambda I)c = 0 \\
\Rightarrow \quad & \begin{pmatrix} \mp\sqrt{2}t & t & t \\ t & \mp\sqrt{2}t & t \\ t & t & \mp\sqrt{2}t \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0 \\
\Rightarrow \quad & \mp\sqrt{2}c_1 + c_2 = 0 \\
& c_1 \mp \sqrt{2}c_2 + c_3 = 0 \\
& c_2 \mp \sqrt{2}c_3 = 0
\end{aligned}
$$

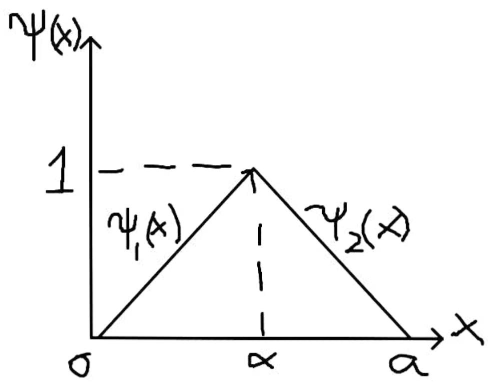
Possible solutions are

$$
|\lambda = \sqrt{2}t\rangle = \frac{1}{2} \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix}
$$

$$
|\lambda = -\sqrt{2}t\rangle = \frac{1}{2} \begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix}
$$

We note that in this case, eigenvalues are symmetrically placed about $\lambda = 0$, which is a sign of particle hole symmetry.

7. Estimate the ground state energy of a particle of mass m in a box with $V = 0$, for $0 \le x \le a$, and $V = \infty$, otherwise, using variational principle. For the purpose, take a wave function consisting of two linear components $\psi_1(x)$ and $\psi_2(x)$ defined by: (i) $\psi_1(0) = 0$, $\psi_1(x = \alpha) = C$ for $0 \le x \le \alpha$, and (ii) $\psi_2(x = \alpha) = C$, $\psi_2(x = a) = 0$, for $\alpha \le x \le a$, where C is the normalization constant, and α is the variational parameter.
   Soln: We estimate the ground state energy of a particle of mass m, in a one dimensional box of length a. We consider the trial function to be a linear function which is zero at x=0 and x=a, and is peaked at x=α, $0 \le \alpha \le a$, where α is the variational parameter.



Clearly

$$\psi(x) = \psi_1(x) = \frac{Nx}{\alpha} \ for \ 0 \le x \le \alpha$$
$$\psi(x) = \psi_2(x) = \frac{N(a-x)}{(a-\alpha)} \ for \ \alpha \le x \le a$$
$$\psi(x) = 0 \ \ elsewhere$$

To obtain normalization constant

$$\int_0^a \psi^2(x)dx = \frac{N^2}{\alpha^2}\int_0^\alpha x^2 dx + \frac{N^2}{(a-\alpha)^2}\int_\alpha^a (a-x)^2 dx$$
$$= \frac{N^2}{3}\alpha + \frac{N^2}{3}(a-\alpha) = 1$$

$$\frac{N^2}{3}a = 1$$
$$N = \sqrt{\frac{3}{a}}$$

$$\Rightarrow \psi_1(x) = \sqrt{\frac{3}{a}}\frac{x}{\alpha}$$
$$\psi_2(x) = \sqrt{\frac{3}{a}}\frac{(a-x)}{(a-\alpha)}$$

Now the standard form

$$E = \langle\psi|H|\psi\rangle = \int \psi^*\Big\{-\frac{\hbar^2}{2m}\nabla^2 + V\Big\}\psi d\tau$$

is not valid here because $\psi'(x)$ is discontinuous at $x = \alpha$. For such cases one uses the alternative expression

$$E = \int \Big\{\frac{\hbar^2}{2m}(\vec{\nabla}\psi^*).(\vec{\nabla}\psi) + V\psi^*\psi\Big\}d\tau$$

which can be obtained by integrating by parts the first term and using the fact that the wave function vanishes at infinity.For the present case $\psi^* = \psi$ and $V = 0$, so that

$$E(\alpha) = \frac{\hbar^2}{2m}\int_0^a \left(\frac{d\psi}{dx}\right)^2 dx$$
$$= \frac{\hbar^2}{2m}\int_0^\alpha \left(\frac{d\psi_1}{dx}\right)^2 dx + \frac{\hbar^2}{2m}\int_\alpha^a \left(\frac{d\psi_2}{dx}\right)^2 dx$$

or

$$E(\alpha) = \frac{\hbar^2}{2m}\left(\frac{3}{a}\right)\frac{1}{\alpha^2}\int_0^\alpha dx + \frac{\hbar^2}{2m}\left(\frac{3}{a}\right)\frac{1}{(a-\alpha)^2}\int_\alpha^a dx$$
$$= \frac{\hbar^2}{2m}\left(\frac{3}{a}\right)\left\{\frac{1}{\alpha} + \frac{1}{a-\alpha}\right\}$$

$$\Rightarrow \frac{dE}{d\alpha} = \frac{\hbar^2}{2m}\left(\frac{3}{a}\right)\left\{-\frac{1}{\alpha^2} + \frac{1}{(a-\alpha)^2}\right\} = 0$$
$$\Rightarrow a - \alpha = \pm\alpha$$

The only meaningful solution is

$$2\alpha = a \Rightarrow \alpha = \frac{a}{2}$$

and

$$E_{min} = \frac{\hbar^2}{2m}\left(\frac{3}{a}\right) \times \frac{4}{a} = \frac{6\hbar^2}{ma^2}$$
$$E_0(exact) = \frac{\hbar^2\pi^2}{2a^2m} \approx \frac{5\hbar^2}{ma^2} \Rightarrow E_{min} > E_0$$

If we plot the true ground state wave function $\psi_0 = \sqrt{\frac{2}{a}}\sin(\frac{\pi x}{a})$ along with the approximate wave function $\psi(x)$ is obtained above, we have

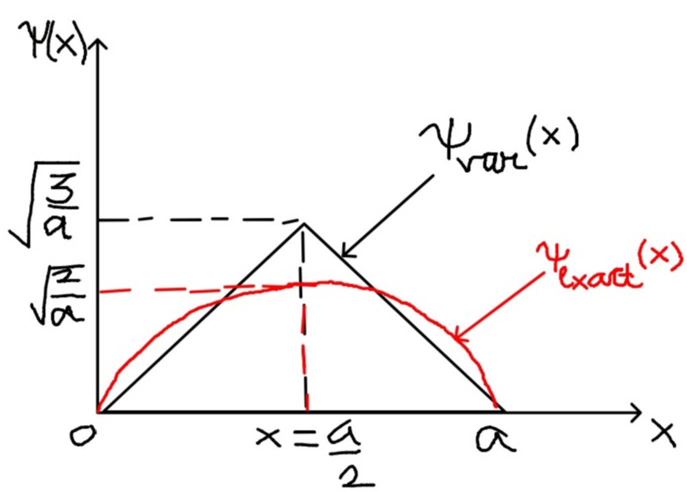


Figure 1: Comparison between the exact and the approximate wave functions

We note that $\alpha = \frac{a}{2}$ obtained through variational principle ensures that the variational wave function peaks at the same $x = \frac{a}{2}$, as an exact wave function.

8. Consider the Hamiltonian of a particle moving in a 1D Gaussian potential well $H = \frac{p^2}{2m} - V_0 e^{-ax^2}$, with V_0 and $a > 0$. Estimate its ground-state energy employing variational principle, with a trial wave function of the form $\psi(x) = Ce^{-\alpha x^2}$, with α as the variational parameter.
Soln: Let us compute

$$E(\alpha) = \int_{-\infty}^{\infty} \left\{ \frac{\hbar^2}{2m} \left(\frac{d\psi}{dx} \right)^2 + V\psi^2 \right\} dx$$

Here $\psi(x) = Ce^{-\alpha x^2}$ where $C = \left(\frac{2\alpha}{\pi}\right)^{1/4}$ was computed in problem 1. Now

$$\frac{d\psi(x)}{dx} = \left(\frac{2\alpha}{\pi} \right)^{1/4} \left\{ -2\alpha x e^{-\alpha x^2} \right\}$$

so

$$\begin{aligned}
E(\alpha) &= \sqrt{\frac{2\alpha}{\pi}} \left\{ \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} 4\alpha^2 x^2 e^{-2\alpha x^2} dx - V_0 \int_{-\infty}^{\infty} e^{-(2\alpha + a)x^2} dx \right\} \\
E(\alpha) &= \sqrt{\frac{2\alpha}{\pi}} \left\{ \frac{\hbar^2}{2m} 4\alpha^2 \frac{1}{2} \sqrt{\frac{\pi}{(2\alpha)^3}} - V_0 \sqrt{\frac{\pi}{2\alpha + a}} \right\} \\
&= \frac{\hbar^2}{2m}\alpha - V_0 \sqrt{\frac{2\alpha}{2\alpha + a}}
\end{aligned}$$

With this

$$\begin{aligned}
\frac{dE}{d\alpha} &= \frac{\hbar^2}{2m} - V_0 \frac{\sqrt{2}}{2\sqrt{\alpha(2\alpha + a)}} + V_0 \frac{2\sqrt{2\alpha}}{2(2\alpha + a)^{3/2}} = 0 \\
&\implies \frac{V_0}{\sqrt{(2\alpha + a)}} \left\{ \frac{1}{\sqrt{2\alpha}} - \frac{\sqrt{2\alpha}}{(2\alpha + a)} \right\} = \frac{\hbar^2}{2m} \\
&\implies \frac{aV_0}{\sqrt{2\alpha(2\alpha + a)^3}} = \frac{\hbar^2}{2m} \\
&\implies 2\alpha(2\alpha + a)^3 = \frac{4m^2 a^2 V_0^2}{\hbar^4}
\end{aligned}$$

After solving this equation for α, we can obtain the value of ground state energy $E(\alpha)$.

9. Using the trial wave function $\psi(\mathbf{r}) = Ce^{-\alpha r}$, where C is the normalization constant, and α is the variational parameter, estimate the ground state energy of the hydrogen atom.
Soln:

$$\psi_\alpha(\mathbf{r}) = Ce^{-\alpha r}$$

$$\int \psi_\alpha^2(\mathbf{r})d^3\mathbf{r} = C^2 \int_0^\infty 4\pi r^2 e^{-2\alpha r} dr = 1$$

$$\Rightarrow 4\pi c^2 \int_0^\infty r^2 e^{-2\alpha r} dr = 1$$

$$\Rightarrow 4\pi C^2 \frac{2!}{(2\alpha)^3} = 1$$

$$\frac{\pi C^2}{\alpha^3} = 1$$

$$C = \sqrt{\frac{\alpha^3}{\pi}}$$

$$\psi(\mathbf{r}) = \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha r}$$

The Hamiltonian for the hydrogen atom is

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r},$$

so that

$$\begin{aligned} E(\alpha) &= \langle \psi(\alpha)|H|\psi(\alpha)\rangle \\ &= \int \left\{ \psi_\alpha \left(-\frac{\hbar^2}{2m}\nabla^2 \psi_\alpha \right) - \frac{e^2}{r}\psi_\alpha^2(\mathbf{r}) \right\} d\mathbf{r} \end{aligned}$$

but

$$-\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) - \frac{\hbar^2}{2mr^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) - \frac{\hbar^2}{2mr^2 \sin^2\theta}\frac{\partial^2}{\partial \varphi^2}$$

As there is no angular dependence of $\psi_\alpha(\mathbf{r})$ since the ground state functionis spherically symmetric, so the last two terms give us zero, so we are left with

$$\begin{aligned}
E(\alpha) &= \int \left\{ \psi_\alpha \left(-\frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi_\alpha}{\partial r} \right) \right) - \frac{e^2}{r} \psi_\alpha^2(\mathbf{r}) \right\} d\mathbf{r} \\
&= \frac{\alpha^3}{\pi} \int \left\{ e^{-\alpha r} \left(-\frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial e^{-\alpha r}}{\partial r} \right) \right) - \frac{e^2}{r} e^{-2\alpha r} \right\} d\mathbf{r} \\
&= -\frac{\hbar^2}{2m} \frac{\alpha^3}{\pi} \int e^{-\alpha r} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial e^{-\alpha r}}{\partial r} \right) \right) d\mathbf{r} - \frac{e^2 \alpha^3}{\pi} \int \frac{e^{-2\alpha r}}{r} d\mathbf{r} \\
&= -\frac{\hbar^2}{2m} \frac{\alpha^3}{\pi} \int e^{-\alpha r} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 [-\alpha e^{-\alpha r}] \right) \right) d\mathbf{r} - \frac{e^2 \alpha^3}{\pi} \int \frac{e^{-2\alpha r}}{r} d\mathbf{r} \\
&= \frac{\hbar^2}{2m} \frac{\alpha^4}{\pi} \int e^{-\alpha r} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 e^{-\alpha r} \right) \right) d\mathbf{r} - \frac{e^2 \alpha^3}{\pi} \int \frac{e^{-2\alpha r}}{r} d\mathbf{r} \\
&= \frac{\hbar^2}{2m} \frac{\alpha^4}{\pi} \int e^{-\alpha r} \left(\frac{1}{r^2} \left[2re^{-\alpha r} - \alpha r^2 e^{-\alpha r} \right] \right) d\mathbf{r} - \frac{e^2 \alpha^3}{\pi} \int \frac{e^{-2\alpha r}}{r} d\mathbf{r} \\
&= \frac{\hbar^2}{2m} \frac{\alpha^4}{\pi} \int e^{-\alpha r} \left(\frac{1}{r^2} \left[2re^{-\alpha r} - \alpha r^2 e^{-\alpha r} \right] \right) 4\pi r^2 dr - \frac{e^2 \alpha^3}{\pi} \int \frac{e^{-2\alpha r}}{r} 4\pi r^2 dr \\
&= \frac{2\hbar^2 \alpha^4}{m} \int e^{-\alpha r} \left(2re^{-\alpha r} - \alpha r^2 e^{-\alpha r} \right) dr - 4\alpha^3 e^2 \int re^{-2\alpha r} r dr \\
&= \frac{2\hbar^2 \alpha^4}{m} \left(2 \int re^{-2\alpha r} dr - \alpha \int r^2 e^{-2\alpha r} dr \right) - 4\alpha^3 e^2 \int re^{-2\alpha r} r dr
\end{aligned}$$

Using the definition of Gamma function

$$\int_0^\infty x^n e^{-ax} dx = \frac{\Gamma(n+1)}{a^{n+1}} \quad where\ a > 0$$

we obtain

$$\begin{aligned}
E(\alpha) &= \frac{2\hbar^2 \alpha^4}{m} \left(2 \left\{ \frac{1!}{(2\alpha)^2} \right\} - \alpha \left\{ \frac{2!}{(2\alpha)^3} \right\} \right) - 4\alpha^3 e^2 \left\{ \frac{1!}{(2\alpha)^2} \right\} \qquad (11) \\
&= \frac{4\hbar^2 \alpha^4}{m} \left(\frac{1}{4\alpha^2} - \frac{1}{8\alpha^2} \right) - \alpha e^2 \\
&= \frac{\hbar^2 \alpha^2}{2m} - \alpha e^2
\end{aligned}$$

$$\begin{aligned}
\frac{dE}{d\alpha} = 0 &\Rightarrow \frac{\hbar^2 \alpha}{m} - e^2 = 0 \\
&\Rightarrow \alpha = \frac{me^2}{\hbar^2} = \frac{1}{a_0} \qquad (12)
\end{aligned}$$

where $a_0 = \frac{\hbar^2}{me^2}$ is the Bohr radius. Substituting Eq.(12) in Eq.(11), we get

$$\begin{aligned} E_{min} &= \frac{\hbar^2}{2m}\left(\frac{m^2e^4}{\hbar^4}\right) - \frac{me^4}{\hbar^2} \\ &= \frac{me^4}{2\hbar^2} - \frac{me^4}{\hbar^2} \\ &= -\frac{me^4}{2\hbar^2} \end{aligned}$$

$$\boxed{E_{min} = -\frac{me^4}{2\hbar^2}}$$

This is the exact value of the ground state energy of the hydrogen atom, obtained after solving the Schrödinger equation.