

Quantum mechanics II, Problems 13 : Time-independent Perturbation Theory and Variational Principle

Solutions

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Problem 1 : Confined quantum Stark effect

We consider an electron of mass m in a one-dimensional potential well of width L , whose infinite barriers are located at $x = \pm L/2$, described by the Hamiltonian \hat{H}_0 . A constant electric field of intensity E is applied to the system, which subjects the electron to the Coulomb force $F = -eE$, resulting in a perturbation $\hat{V}(\hat{x}) = F\hat{x}$.

1. Sketch the total potential experienced by the electron for $F > 0$.

Solution : The total potential is an infinite barrier potential with a sloped bottom along a line with positive slope $F = -eE > 0$ ($E < 0$).

2. Provide the Hamiltonian \hat{H}_0 . Recall the eigenenergies E_n and wavefunctions $\varphi_n(x)$ ($n = 1, 2, \dots$) of the unperturbed electron, i.e., when $F = 0$, distinguishing between even and odd n cases.

Solution : The perturbed system Hamiltonian is written :

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m} + V_0(\hat{x})}_{=\hat{H}_0} + F\hat{x}, \quad (1)$$

where $V_0(\hat{x})$ is the potential well. In the position space, it is given by

$$V_0(x) = \begin{cases} 0 & \text{if } |x| \leq L/2, \\ \infty & \text{else.} \end{cases} \quad (2)$$

In the case where $F = 0$ the eigenenergies of the confined electron are

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2mL^2}, n > 0 \quad (3)$$

and the corresponding wavefunctions

$$\varphi_n(x) = \sqrt{\frac{2}{L}} \cos\left(\frac{n\pi}{L}x\right), \text{ if } n \text{ is odd} \quad (4)$$

$$\varphi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right), \text{ if } n \text{ is even.} \quad (5)$$

Recall that these results are obtained by solving Schrödinger equation of a free electron (i.e. with Hamiltonian $\frac{\hat{p}^2}{2m}$) inside the potential well. Then, the potential barrier implies $\phi_n(x) = 0$ for $|x| \geq L/2$. In particular, the wavefunctions inside the well must match the bound conditions i.e. $\phi_n(\pm L/2) = 0$ to avoid discontinuity. (see course or e.g. "Particle in a box - Wikipedia")

3. Calculate the first-order energy correction $E_1^{(1)}$ for the ground state in the case $F \neq 0$. What do you notice?

Solution : In the case where $F \neq 0$, the energy correction of the ground state is the average value of the perturbation operator on the unperturbed states, which is given by :

$$E_1^{(1)} = \int_{-L/2}^{+L/2} \varphi_1^*(x) Fx \varphi_1(x) dx = \frac{2F}{L} \int_{-L/2}^{+L/2} x \cos^2\left(\frac{\pi}{L}x\right) dx \quad (6)$$

Directly by noticing that $x \mapsto x \cos^2(x)$ is odd, or by integrating by parts, we find $E_1^{(1)} = 0$.

4. Derive the first-order energy corrections $E_n^{(1)}$ for excited states with $n > 1$.

Solution : The energy correction of the first 2 excited states is given by

$$E_2^{(1)} = \frac{2F}{L} \int_{-L/2}^{+L/2} x \sin^2\left(\frac{2\pi}{L}x\right) dx \quad (7)$$

$$E_3^{(1)} = \frac{2F}{L} \int_{-L/2}^{+L/2} x \cos^2\left(\frac{3\pi}{L}x\right) dx \quad (8)$$

and also involve odd integrands, which is indeed the case for any n , so we simply have $E_n^{(1)} = 0$ for all n .

5. Now calculate the second-order energy correction $E_1^{(2)}$ for the ground state (exploit the wavefunction parity). For the sums over intermediate states, consider only the states $\varphi_1(x)$ and $\varphi_2(x)$, and denote by V_{21} the matrix element of the perturbation, computed between these two states.

Solution : The energy correction $E_1^{(2)}$ of the ground state at order 2 involves non-zero matrix elements

$$V_{j1} = \frac{2F}{L} \int_{-L/2}^{+L/2} x \sin\left(\frac{j\pi}{L}x\right) \cos\left(\frac{\pi}{L}x\right) dx \quad (9)$$

only if j is even. Indeed, in cases where j is odd, the elements are zero due to parity (i.e. as $x \mapsto x \cos\left(\frac{j\pi}{L}x\right) \cos\left(\frac{\pi}{L}x\right)$ is odd). If we consider only the coupling with the first excited level, namely $j = 2$, the correction to the ground state is simply

$$E_1^{(2)} = -\frac{V_{21}^* V_{21}}{E_2 - E_1} \quad (10)$$

with

$$V_{21} = \frac{16}{9\pi^2} FL \quad (11)$$

using the identity $\sin(a) \cos(b) = \frac{1}{2}(\sin(a+b) + \sin(a-b))$ and by integrating terms of the form $x \sin(wx)$ by part (notice that $x \sin(wx) = \frac{d}{dx} \left(\frac{\sin(wx) - wx \cos(wx)}{w^2} \right)$). And so finally

$$E_1^{(2)} = -\frac{256}{243\pi^4} \frac{F^2 L^2}{E_1} . \quad (12)$$

6. Intuitively and qualitatively depict the shape of the wavefunction of the ground state in the total potential.

Solution : The wavefunction of the ground state becomes asymmetric and localizes where the potential is the weakest.

Problem 2 : Degenerate Perturbation Theory for a 3-State System

We consider the following Hamiltonian acting on a spin 1 :

$$\hat{H} = -D\hat{S}_z^2 + \lambda B\hat{S}_x \quad (13)$$

This is a model that can be realistic in certain materials. The first term represents an anisotropy, and the second a magnetic field along the x direction. We propose to diagonalize this Hamiltonian by considering the term λBS_x as a perturbation. Subsequently, we assume that B and D are non-zero.

1. Under what condition does the Hamiltonian commute with \hat{S}_z ? In this case, give the eigenvalues and eigenvectors of \hat{H} .

Solution : By definition of the angular momentum operators, the commutator of H with S_z yields

$$[H, S_z] = -D[S_z^2, S_z] + \lambda B[S_x, S_z] = -i\hbar\lambda BS_y \quad (14)$$

Assuming B is non-zero, $[H, S_z] = 0$ only if $\lambda = 0$. In this case, the eigenstates of S_z are also eigenstates of H , and applying H to them gives their energy. We have $S_z^2|m\rangle = \hbar m S_z|m\rangle = \hbar^2 m^2|m\rangle$, hence the eigenstates and eigenenergies of H are :

$$|0\rangle \equiv |m = 0\rangle : \quad E = 0 \quad (15)$$

$$|\bar{1}\rangle \equiv |m = -1\rangle : \quad E = -D\hbar^2 \quad (16)$$

$$|1\rangle \equiv |m = +1\rangle : \quad E = -D\hbar^2 \quad (17)$$

The eigenenergy $-D\hbar^2$ is thus two-fold degenerate.

2. Subsequently, we consider $\lambda \neq 0$. Write down the matrix of the Hamiltonian in the basis of eigenstates of S_z . Using second order perturbation theory, compute the energy correction for the state $|m = 0\rangle$. Calculate the correction to the associated eigenvector, to first order in perturbation theory.

Solution : We write the Hamiltonian in the basis $\mathcal{B}_1 = \{|\bar{1}\rangle, |0\rangle, |1\rangle\}$. To determine the matrix of the operator S_x , we use the formula $S_x = \frac{1}{2}(S^+ + S^-)$ and

$$S^\pm |SM\rangle = \hbar\sqrt{S(S+1) - M(M\pm 1)} |S, M\pm 1\rangle \quad (18)$$

It is then easy to apply S_x on the basis states :

$$S_x|\bar{1}\rangle = \frac{\hbar}{2}\sqrt{2}|0\rangle = \frac{\hbar}{\sqrt{2}}|0\rangle \quad (19)$$

$$S_x|0\rangle = \frac{\hbar}{2}[\sqrt{2}|1\rangle + \sqrt{2}|\bar{1}\rangle] = \frac{\hbar}{\sqrt{2}}[|1\rangle + |\bar{1}\rangle] \quad (20)$$

$$S_x|1\rangle = \frac{\hbar}{2}\sqrt{2}|0\rangle = \frac{\hbar}{\sqrt{2}}|0\rangle \quad (21)$$

The action of S_z^2 is simply $S_z^2|\bar{1}\rangle = \hbar^2|\bar{1}\rangle$, $S_z^2|0\rangle = 0$, and $S_z^2|1\rangle = \hbar^2|1\rangle$. The matrix of the Hamiltonian is then equal to

$$H = \begin{pmatrix} -D\hbar^2 & \lambda B \frac{\hbar}{\sqrt{2}} & 0 \\ \lambda B \frac{\hbar}{\sqrt{2}} & 0 & \lambda B \frac{\hbar}{\sqrt{2}} \\ 0 & \lambda B \frac{\hbar}{\sqrt{2}} & -D\hbar^2 \end{pmatrix} \quad (22)$$

Since the energy level $\epsilon_1 = 0$ is non-degenerate, for $\lambda = 0$, we can use non-degenerate perturbation theory. According to the course, the first-order correction is (Eq. 8.9)

$$E_1^{(1)} = B\langle 0|S_x|0\rangle = 0 \quad (23)$$

At second order, in the Rayleigh-Schrödinger formalism (Eq. 8.22) :

$$E_1^{(2)} = \frac{|\langle \bar{1}|BS_x|0\rangle|^2}{0 - (-D\hbar^2)} + \frac{|\langle 1|BS_x|0\rangle|^2}{0 - (-D\hbar^2)} = B^2/D \quad (24)$$

Notice that in this calculation, λ does not appear. It is introduced in the energy correction (Eq. 10.9) :

$$E_1 = \underbrace{\epsilon_0}_{=0} + \lambda \underbrace{E_1^{(1)}}_{=0} + \lambda^2 E_1^{(2)} + \mathcal{O}(\lambda^3), \quad (25)$$

so

$$E_1 = \lambda^2 B^2/D + \mathcal{O}(\lambda^3) \quad (26)$$

The correction to the eigenvector to first order is given by Eq.(10.16) :

$$\langle \bar{1}|\Psi_1^{(1)}\rangle = \frac{\langle \bar{1}|BS_x|0\rangle}{D\hbar^2} = \frac{B}{\sqrt{2}D\hbar} \quad (27)$$

$$\langle 1|\Psi_1^{(1)}\rangle = \frac{\langle 1|BS_x|0\rangle}{D\hbar^2} = \frac{B}{\sqrt{2}D\hbar} \quad (28)$$

Therefore, to first order in λ , the eigenvector associated with the energy $E_1 = \lambda^2 B^2/D$ is (Eq. 10.9) :

$$|\Psi_1\rangle = |0\rangle + \lambda \left(\langle \bar{1}|\Psi_1^{(1)}\rangle |\bar{1}\rangle + \langle 1|\Psi_1^{(1)}\rangle |1\rangle \right) + \mathcal{O}(\lambda^2)$$

Finally,

$$|\Psi_1\rangle = |0\rangle + \frac{1}{\sqrt{2}} \frac{B\lambda}{D\hbar} \left(|\bar{1}\rangle + |1\rangle \right) + \mathcal{O}(\lambda^2) \quad (29)$$

3. To calculate the effect of the perturbation on the other two states, it is necessary to use degenerate perturbation theory. What is the matrix of the operator \hat{S}_x in the degenerate subspace? Deduce that the first-order correction is zero.

Solution : According to degenerate perturbation theory, the first-order correction to the energy is given by the eigenvalues of the restriction \tilde{V} of $V = \lambda BS_x$ to the subspace $\{|\bar{1}\rangle, |1\rangle\}$ (Eq. 8.41). This matrix is written as :

$$\tilde{V} = \begin{pmatrix} \langle \bar{1}|V|\bar{1}\rangle & \langle \bar{1}|V|1\rangle \\ \langle 1|V|\bar{1}\rangle & \langle 1|V|1\rangle \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \quad (30)$$

Here, the eigenvalues of \tilde{V} are 0, and therefore the first-order correction to the energy is zero.

Remarque

In the general case where the matrix \tilde{V} has two different eigenvalues, it lifts the degeneracy and allows us to find the eigenvectors $|\Psi_{2,3}^{(0)}\rangle$ which will be the starting point for the perturbation expansion of the vectors $|\Psi_{2,3}\rangle$. Here, we are in the particular case where the degenerate subspace for H_0 is also degenerate for \tilde{V} . Therefore, we will need to go to the next order to find the desired eigenvectors.

Problem 3 : Potential well

Summary The aim of this exercise is to understand the principle of the variational method. We consider the problem of an infinite 1D potential well, defined by :

$$V(x) = \begin{cases} 0 & \text{if } |x| < a \\ +\infty & \text{if } |x| \geq a \end{cases}$$

where the ground state is given by :

$$E_0 = \frac{\hbar^2}{2m} \frac{\pi^2}{4a^2} \quad (31)$$

We propose to seek an approximate value of the ground state energy by the variational method. To this end, we consider the functions :

$$\psi_\lambda(x) = \begin{cases} a^\lambda - |x|^\lambda & \text{si } |x| < a \\ 0 & \text{si } |x| \geq a \end{cases} \quad (32)$$

We recall that the condition $\lambda > 1$ is imposed because the derivative of a wavefunction is generally continuous at all points where the potential is continuous (or has only a finite jump).

1. Calculate $\langle \psi_\lambda | \psi_\lambda \rangle$.

Solution : We start by calculating $\langle \psi_\lambda | \psi_\lambda \rangle$:

$$\begin{aligned} \langle \psi_\lambda | \psi_\lambda \rangle &= \int_{\mathbb{R}} |\psi_\lambda(x)|^2 dx = \int_{-a}^a (a^\lambda - |x|^\lambda)^2 dx = 2 \int_0^a (a^\lambda - x^\lambda)^2 dx \\ &= 2 \left(a^{2\lambda+1} - 2a^\lambda \frac{a^{\lambda+1}}{\lambda+1} + \frac{a^{2\lambda+1}}{2\lambda+1} \right) = 4a^{2\lambda+1} \frac{\lambda^2}{(\lambda+1)(2\lambda+1)} \end{aligned} \quad (33)$$

2. Determine the value of λ that minimizes the energy. Compare with the exact ground state energy and deduce the relative error.

Solution : Calculate first :

$$\begin{aligned} \langle \psi_\lambda | H | \psi_\lambda \rangle &= \int_{\mathbb{R}} \psi_\lambda^*(x) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \psi_\lambda(x) dx \\ &= -\frac{\hbar^2}{2m} 2 \int_0^a (a^\lambda - x^\lambda) \frac{d^2}{dx^2} (a^\lambda - x^\lambda) dx \\ &= \frac{\hbar^2}{2m} 2 \int_0^a (a^\lambda - x^\lambda) \lambda(\lambda-1) x^{\lambda-2} dx \\ &= \frac{\hbar^2}{2m} 2 \left(a^\lambda \lambda(\lambda-1) \frac{a^{\lambda-1}}{\lambda-1} - \lambda(\lambda-1) \frac{a^{2\lambda-1}}{2\lambda-1} \right) \\ &= \frac{\hbar^2}{m} a^{2\lambda-1} \frac{\lambda^2}{2\lambda-1} \end{aligned} \quad (34)$$

With (33) and (34), we can calculate the average value of the energy for the state $|\psi_\lambda\rangle$, which is given by :

$$E_{\text{var}}(\lambda) = \frac{\langle \psi_\lambda | H | \psi_\lambda \rangle}{\langle \psi_\lambda | \psi_\lambda \rangle} = \frac{\hbar^2}{m} \frac{1}{4a^2} \frac{(\lambda+1)(2\lambda+1)}{2\lambda-1} = \frac{\hbar^2}{m} \frac{1}{4a^2} \frac{2\lambda^2+3\lambda+1}{2\lambda-1} \quad (35)$$

The minimum energy is therefore achieved for the value of λ that minimizes $\frac{2\lambda^2+3\lambda+1}{2\lambda-1}$. To calculate this λ , we set :

$$\frac{\partial}{\partial \lambda} \frac{2\lambda^2+3\lambda+1}{2\lambda-1} = \frac{(4\lambda+3)(2\lambda-1) - 2(2\lambda^2+3\lambda+1)}{(2\lambda-1)^2} = \frac{4\lambda^2-4\lambda-5}{(2\lambda-1)^2}$$

By requiring that the numerator vanishes, we find the roots $\lambda_{+,-} = \frac{1 \pm \sqrt{6}}{2}$, and since we want $\lambda > 1$, we keep the positive root :

$$\lambda_+ = \frac{1 + \sqrt{6}}{2} \approx 1.72$$

As the function $\frac{2\lambda^2+3\lambda+1}{2\lambda-1}$ diverges as $\lambda \rightarrow \infty$, while its derivative is negative as $\lambda \rightarrow 1$, we can see that it reaches its minimum at the point λ_+ . By plugging λ_+ into (35), we find :

$$E_{\text{var}}(\lambda_+) = \frac{\hbar^2}{2m} \frac{1}{4a^2} (5 + 2\sqrt{6})$$

Comparing with the exact energy of the ground state :

$$E_0 = \frac{\hbar^2}{2m} \frac{\pi^2}{4a^2}$$

gives a relative error of :

$$\frac{E_{\text{var}}(\lambda_+)}{E_0} = \frac{5 + 2\sqrt{6}}{\pi^2} \approx 1.00298$$

So we see that our variational function - albeit very simple - gives an energy remarkably close to the exact ground state energy. Therefore, we expect $|\psi_{\lambda_+}\rangle$ to accurately describe the physics of the ground state.