

Answer all parts together else they will not be checked.

1. True/False: One line reason. Correct statement if false. (5 × 2)

- Every linear combination of solutions of the time-dependent Schrodinger equation is a solution of this equation.
- The eigenvalues of a diagonal matrix are equal to the diagonal elements, a_{ii} .
- If two Hermitian operators do not commute, they cannot possess any common eigenfunctions.
- For every system of several fermions, interchange of the labels of two fermions in the wavefunction must multiply the wavefunction by -1 .
- When perturbative correction is applied on the ground state, the second order correction to energy is always positive.

Answer 1:

- True: Show that $-\frac{\hbar}{i} \frac{\partial \chi}{\partial t} = \hat{H}\chi$ is satisfied by the linear combination of solutions $e^{-iEt/\hbar}\psi(q)$
- True: Show in matrix form $\hat{H}C = WC$
- False: They can possess some common eigenfunctions. Correct statement: If two Hermitian operators do not commute, they cannot possess complete common set of eigenfunctions.
- True: Pauli's principle states so.
- False: $E_0^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | \hat{H}' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}$ shows the denominator is always negative while the numerator is always positive. Correct statement: When perturbative correction is applied on the ground state, the second order correction to energy is always negative.

2. Parity operator (3+5+2)

The parity operator $\hat{\Pi}$ converts a function $f(x, y, z)$ to $f(-x, -y, -z)$. Find the eigenvalues of the operator. Under what conditions does the operator commute with the Hamiltonian? A system that has been taught to you has a common set of eigenfunctions with $\hat{\Pi}$. Show explicitly that the first two states of this system are also eigenfunctions of $\hat{\Pi}$.

Answer 2:

$\hat{\Pi}^2 f(x, y, z) = 1 \cdot f(x, y, z)$. Therefore, the eigenvalues of $\hat{\Pi}$ are ± 1 .

$$\hat{\Pi}\hat{H}f - \hat{H}\hat{\Pi}f = \hat{\Pi}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x, y, z)\right)f - \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x, y, z)\right)\hat{\Pi}f$$

This can be broken up as

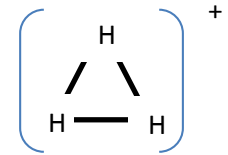
$$\begin{aligned}
& \hat{\Pi} \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) f + \hat{\Pi} V(x, y, z) f - \left(\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \hat{\Pi} f + V(x, y, z) \hat{\Pi} f \right) \\
&= -\frac{\hbar^2}{2m} \frac{\partial}{\partial(-x)} \frac{\partial}{\partial(-x)} f(-x, -y, -z) + V(-x, -y, -z) f(-x, -y, -z) \\
&\quad + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} f(-x, -y, -z) + V(x, y, z) f(-x, -y, -z) \\
&= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} f(-x, -y, -z) + V(-x, -y, -z) f(x, y, z) \\
&\quad + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} f(-x, -y, -z) - V(x, y, z) f(-x, -y, -z) \\
&= V(-x, -y, -z) f(-x, -y, -z) - V(x, y, z) f(-x, -y, -z)
\end{aligned}$$

This can go to zero only when $V(-x, -y, -z) = V(x, y, z)$. The potential must be an even function.

The system taught to you is the Harmonic oscillator where the potential energy is an even function. Show that $\hat{\Pi}\psi_0 = +1\psi_0$ and $\hat{\Pi}\psi_1 = -1\psi_1$

3. Huckel M.O.T. (8)

Determine whether the linear state (H – H – H⁺) or the triangular state of H₃⁺ is more stable.



Answer 3:

Write the secular determinants

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} \text{ for the linear system gives } E = \alpha \pm \sqrt{2} \beta$$

and $\begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{vmatrix}$ for the triangular system, $E = \alpha + 2\beta$ and $E = \alpha - \beta$. Fill up two electrons and see that the triangular system is lower in energy.

4. Harmonic Oscillator (5 × 2)

A particle is in the state described by

$$\psi = N \left(\frac{\alpha}{\pi} \right)^{1/4} \left[\frac{4}{2\sqrt{2}} \xi^2 + \frac{4}{\sqrt{2}} \xi - \frac{2}{2\sqrt{2}} \right] \exp(-\alpha x^2/2)$$

where, $\xi = \alpha^{1/2} x$.

- a) What is the probability that the particle will be found in the ground state? What is the probability that it is found in the first excited state?

- b) Is this state an odd or an even function about x ? Plot it.
- c) Determine the value of the normalization constant N .
- d) Determine the average energy of the state.
- e) How would this energy change in the presence of a weak electric field of magnitude f applied along the $+x$ direction if the particle has a charge $-e$? (Use only first order perturbation correction.)

Answer 4:

The first thing to realize is that ψ is not an eigenfunction since the eigenfunctions contain either odd or even powers of ξ only. Therefore, it is a linear combination of eigenfunctions. Looking at the table of Hermite polynomials given below, the wavefunction can be written as a linear combination of the two eigenfunctions, $\psi = 2\psi_1 + \psi_2$.

- a) Since ψ_0 is not in the sum above, the probability that the particle be found in the ground state is zero. For first excited state the probability is the square of the coefficient for the normalized wavefunction i.e. $4/5$. You get the value 5 when you evaluate N .
- b) Neither odd nor even. Sum up the two eigenfunctions and see.
- c) Normalization constant is $1/\sqrt{\sum c_i^2}$. So it comes out $1/\sqrt{5}$. The two eigenfunctions are normalized so you need not carry out any integrations.
- d) Average energy is given by $\sum c_i^2 E_i$ when the wavefunction is normalized. Plug in the values of the energies of the 1st and 2nd excited states.
- e) First order perturbation correction is given by $\langle \psi | \hat{H}' | \psi \rangle$. Since it is a multiplication of odd and even functions the integral over all space turns out to be zero.

5. Approximate Methods (5+7)

- a) Calculate the first order correction to energy for a particle in a 1-D box of length a with the potential $V = x/a$ inside the box and $V = \infty$ outside.
- b) Consider the one-particle, 1D system with potential energy

$$V = \frac{\hbar^2}{ml^2} \quad \text{for} \quad \frac{1}{4}l < x < \frac{3}{4}l, \quad V = 0 \quad \text{for} \quad 0 \leq x \leq \frac{1}{4}l \quad \text{and} \quad \frac{3}{4}l \leq x \leq l$$

and $V = \infty$ elsewhere. Use the trial variation function, $\phi_1 = \sqrt{2/l} \sin \pi x/l$ to estimate the ground state energy. What result do you expect (to first order) if the potential $\hbar^2/ml^2$ is treated as a perturbation? Show without actually doing the perturbative calculation.

Answer 5:

- a) First order correction is given by $\langle \psi | \hat{H}' | \psi \rangle$. This gives

$$\int_0^a \sqrt{2/a} \sin \pi x/a \cdot x/a \cdot \sqrt{2/a} \sin \pi x/a \, dx$$

The integral can be calculated from the formula given below.

- b) Variation theorem gives $W = \langle \phi_1 | \hat{H} | \phi_1 \rangle / \langle \phi_1 | \phi_1 \rangle$. Since ϕ_1 is the normalized ground state eigenfunction for the P-I-B use only the numerator.

$$W = \int_0^l \phi_1 \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \phi_1 dx + \int_{1/4l}^{3/4l} \phi_1 \left(\frac{\hbar^2}{ml^2} \right) \phi_1 dx$$

The first term gives the ground state energy for the P-I-B, i.e. $\hbar^2/8ml^2$. The second term needs to be evaluated.

$$\begin{aligned} \int_{1/4l}^{3/4l} \phi_1 \left(\frac{\hbar^2}{ml^2} \right) \phi_1 dx &= \frac{2\hbar^2}{ml^3} \int_{1/4l}^{3/4l} \sin^2 \frac{\pi x}{l} dx = \frac{2\hbar^2}{ml^3} \int_{1/4l}^{3/4l} \frac{1 - \cos \frac{2\pi x}{l}}{2} dx \\ &= \frac{\hbar^2}{ml^3} \left[x - \sin \frac{2\pi x}{2l} \right]_{1/4l}^{3/4l} = \frac{\hbar^2}{ml^3} \left[\frac{l}{2} - \sin \frac{3\pi}{4} + \sin \frac{\pi}{4} \right] = \frac{\hbar^2}{2ml^2} \end{aligned}$$

Look at the first equation $W = \int_0^l \phi_1 \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \phi_1 dx + \int_{1/4l}^{3/4l} \phi_1 \left(\frac{\hbar^2}{ml^2} \right) \phi_1 dx$

This can be written as $\langle \phi_1 | \hat{H}^0 | \phi_1 \rangle + \langle \phi_1 | \hat{H}' | \phi_1 \rangle$. Therefore the perturbation theory to the first order must give exactly the same result as the variation method.

Useful information

$$h = 6.626 \times 10^{-34} \text{ J.s}, \quad m_e = 9.1 \times 10^{-31} \text{ kg}, \quad \epsilon_0 = 8.854 \times 10^{-12} \text{ F.m}^{-1}, \quad c = 3 \times 10^8 \text{ m.s}^{-1}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}, \quad e = 1.6 \times 10^{-19} \text{ C}, \quad m_p = 1.67 \times 10^{-27} \text{ kg}$$

Harmonic Oscillator

$$\psi_v(x) = N_v H_v(\alpha^{1/2} x) e^{-\alpha x^2/2}$$

$$\alpha = \left(\frac{k\mu}{\hbar^2} \right)^{1/2}$$

$$N_v = \frac{1}{(2^v v!)^{1/2}} \left(\frac{\alpha}{\pi} \right)^{1/4}$$

v	$H_v(\xi)$
0	1
1	2ξ
2	$4\xi^2 - 2$
3	$8\xi^3 - 12\xi$
4	$16\xi^4 - 48\xi^2 + 12$
5	$32\xi^5 - 160\xi^3 + 120\xi$

Useful integral

$$\int x \sin^2 ax \, dx = \frac{x^2}{4} - \frac{x}{4a} \sin 2ax - \frac{1}{8a^2} \cos 2ax + C$$