

1. **He (2 + 3)**

Write the Hamiltonian for the He atom. Can the solution to the Schrödinger equation be of the form $\psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = \phi_1(r_1, \theta_1, \phi_1)\phi_2(r_2, \theta_2, \phi_2)$? Why or why not? Give a brief justification.

$$-\frac{\hbar^2}{2m_N} \nabla_N^2 - \frac{\hbar^2}{2m_{e1}} \nabla_{e1}^2 - \frac{\hbar^2}{2m_{e2}} \nabla_{e2}^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

$\psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = \phi_1(r_1, \theta_1, \phi_1)\phi_2(r_2, \theta_2, \phi_2)$ cannot be a solution as the inter-electronic repulsion term is missing.

2. **True/False with one line justification (6× 1)**

- Two linearly independent eigenfunctions of the same Hermitian operator are always orthogonal to each other
TRUE: You can show the orthogonality of the eigenfunctions using different eigenvalues as taught in class.
- The normalized state function ψ is dimensionless (i.e. has no units).
FALSE: See for example, the PIB wavefunctions
- The relation $\langle f|\hat{A}|g\rangle = \langle g|\hat{A}|f\rangle^*$ is only valid when f and g are eigenfunctions of the Hermitian operator $\hat{A}$.
FALSE: The definition of Hermitian is for any state function
- The eigenvalues of a diagonal matrix are equal to the diagonal elements.
TRUE: Show a diagonal matrix and evaluate its eigenvalues
- The non-degenerate perturbation theory formula $E^{(1)} = \langle \psi^{(0)}|\hat{H}'|\psi^{(0)}\rangle$ applies only to the ground state.
FALSE: There is no mention of the G.S.
- ψ_{120} is an eigenfunction of the H-atom.
FALSE: There is no 1d orbital

3. **Fill in the blanks (4 × 1)**

- Every linear combination of solutions of the time-dependent Schrödinger equation is a solution to this equation.
- Every non-zero linear combination of two eigenvectors that corresponds to the same eigenvalue of a matrix is an eigenfunction of that matrix.
- When ψ is an eigenfunction of operator $\hat{B}$ with eigenvalue b_k , we are definite/certain to observe the value b_k when the property $\hat{B}$ is measured.
- The $\hat{L}^2$ eigenvalues are degenerate except for $l = 0$.

4. **Partilce-on-a-ring** (2+3 + 2 + 3)

The six π electrons of benzene can be modeled as independent, free particles on a ring with a radius of 134 pm. The Hamiltonian for a π electron is $-\frac{\hbar^2}{2mr^2} \frac{\partial^2}{\partial \phi^2}$.

a) What are the boundary conditions satisfied by the solutions to the Schrödinger equation?

$$\psi(\phi) = \psi(\phi + 2\pi)$$

b) What are the solutions?

$$-\frac{\hbar^2}{2mr^2} \frac{\partial^2 \psi}{\partial \phi^2} = E\psi$$

$$\frac{\partial^2 \psi}{\partial \phi^2} = -\frac{2mr^2 E}{\hbar^2} \psi$$

$$\frac{\partial^2 \psi}{\partial \phi^2} + k^2 \psi = 0$$

You know the solutions to this and you get $\psi = Ae^{\pm ik\phi}$. Normalize to $A = 1/\sqrt{2}$.

c) Write the energies and quantum numbers of the three lowest levels.

Apply boundary condition to get $k = 0, \pm 1, \pm 2 \dots$ Three lowest levels are for $k = 0, \pm 1$.

Substitute the expression for energy from above and get $E = \frac{k^2 \hbar^2}{2I}$ and write the energies for these three levels.

d) Calculate the energy required for the lowest absorption to occur?

$$m_e = 9.109 \times 10^{-31} \text{kg}, h = 6.626 \times 10^{-34} \text{J s}^{-1}, c = 3.0 \times 10^8 \text{ms}^{-1}$$

The lowest energy transition corresponds to $k = 1$ to $k = 2$ state. Evaluate.

5. **Variation** (5 + 5)

- a) Try the guess function $\psi = x$ for the 1-D particle in a box confined between $0 \leq x \leq l$. Use the normalized function. Does it give a reasonable answer? Why?

$$W = \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle$$

$$W = \langle x | -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} x \rangle = 0$$

(double differential of x gives 0)

Normalize (evaluate $\langle x | x \rangle$ in the limit 0 to l) to get $\sqrt{\frac{3}{l^3}}$

The true energy for PIB GS is $\hbar^2/8ml^2$ so a value lower than that is unacceptable. It can only be lower if the guess is not well-behaved. See that $\psi = x$ does not satisfy the boundary conditions. It is not zero at $x = l$.

- b) A 1-particle, 1-D P-I-B system has $V = V_0$ inside the box of length, l , and $V = \infty$ outside. Use a linear combination of the ground state and the first excited state P-I-B eigenfunctions that have been taught to you, as the guess function, i.e. $c_1\psi_1 + c_2\psi_2$. Find out the values of the coefficients and the energy. Comment on the result and discuss.

$$\begin{aligned} & \langle c_1\psi_1 + c_2\psi_2 | -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V_0 | c_1\psi_1 + c_2\psi_2 \rangle / \langle c_1\psi_1 + c_2\psi_2 | c_1\psi_1 + c_2\psi_2 \rangle \\ & \langle c_1\psi_1 + c_2\psi_2 | c_1(E_1 + V_0)\psi_1 + c_2(E_2 + V_0)\psi_2 \rangle / \langle c_1\psi_1 + c_2\psi_2 | c_1\psi_1 + c_2\psi_2 \rangle \end{aligned}$$

Since the eigenfunctions are orthonormalized,

Work out the denominator to get $c_1^2 + c_2^2$

numerator is

$$\begin{aligned} & \langle c_1\psi_1 + c_2\psi_2 | c_1(E_1 + V_0)\psi_1 + c_2(E_2 + V_0)\psi_2 \rangle \\ & c_1^2(E_1 + V_0) + c_2^2(E_2 + V_0) \end{aligned}$$

If minimized w.r.t. either c_1 or c_2 , you can see the lowest possible value is $E_1 + V_0$. Any contribution from E_2 would result in a higher value. So c_2 goes to zero and $c_1 = 1$.

The reason is that we are looking at an infinitely deep well and its our choice where to place the zero of the potential energy. So the results would be identical to the case with $V_0 = 0$, except that they are shifted by whatever value of V_0 you wish to specify.

6. **Perturbation** (5)

For an anharmonic oscillator whose Hamiltonian is described by $\hat{H} = \hat{H}^0 + cx^3 + dx^4$, where $\hat{H}^0$ is the Hamiltonian for the harmonic oscillator, evaluate the first order correction to energy

for the ground state. The unperturbed G.S. eigenfunction is given by $(\alpha/\pi)^{1/4} e^{-\alpha x^2/2}$, where $\alpha = 2\pi\nu m/\hbar$.

Useful integral:

$$\int_0^\infty x^{2n} e^{-bx^2} dx = \frac{(2n)!}{2^{2n+1} n!} \left(\frac{\pi}{b^{2n+1}} \right)^{1/2}$$

$$\left\langle (\alpha/\pi)^{1/4} e^{-\alpha x^2/2} \left| cx^3 + dx^4 \right| (\alpha/\pi)^{1/4} e^{-\alpha x^2/2} \right\rangle$$

The first term gives zero because its an odd function.

The second term gives the form of the integral above. Plug in the values and get $3dh^2/64\pi^4\nu^2m^2$