PC3602

ONE HOUR THIRTY MINUTES

A list of basic formulas is included.

UNIVERSITY OF MANCHESTER

Quantum Mechanics of Atoms and Molecules

XXXX May/June 2008, xx.xx-xx.xx.

Answer **ALL** parts of question 1 and **TWO** other questions

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Electronic calculators may be used, provided that they cannot store text.

The numbers are given as a guide to the relative weights of the different parts of each question.

BASIC FORMULAS

The following formulas may be used freely as required.

1. Perturbation Theory: If $\hat{H} = \hat{H}_0 + \hat{V}$, we have, in the usual notation

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots$$
$$\psi_n = \psi_n^{(0)} + \psi_n^{(1)} + \cdots$$

where $E_n^{(0)}$ and $\psi_n^{(0)}$ ($\to |n\rangle$ in Dirac notation) are the energy eigenvalues and eigenstates of $\hat{H}_0$ respectively,

$$E_n^{(1)} = V_{nn}, \quad E_n^{(2)} = \sum_{m \neq n} \frac{|V_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}, \quad \psi_n^{(1)} = \sum_{m \neq n} \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}$$

and $V_{mn} = \langle m| \hat{V} |n\rangle$.

2. Time-dependent Perturbation Theory: If $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$, the first-order probability amplitude for the transition from state $|1\rangle$ at $t = 0$ to state $|2\rangle$ at $t > 0$ is given by

$$c(t) = \frac{1}{i\hbar} \int_0^t \langle 2| \hat{V}(t') |1\rangle e^{i\omega t'} dt'$$

where $\hbar\omega = E_2 - E_1$ is the energy difference between the two eigenstates of $\hat{H}_0$.

3. Special integrals: For $a > 0$,

$$\int_0^\infty e^{-ax^2} x^{2n} dx = \frac{1 \cdot 3 \cdot \ldots \cdot (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$$
$$\int_0^\infty e^{-ax} x^n dx = \frac{n!}{a^{n+1}} \, .$$

4. Laplacian operator:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\hat{L}^2}{\hbar^2 r^2}$$

where $\hat{L}^2$ is the square of angular momentum operator

$$\hat{L}^2 = -\hbar^2 \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right) \, .$$