Physical Chemistry Cume
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In this cume, you can show how you understand principles of quantum and statistical mechanics.

1. a) Why do we use linear Hermitian operators in quantum mechanics? Explain some of their properties.

   b) Can we prepare a quantum particle in a state of well defined coordinate and momentum? Why? How?

   c) What are the origins of correlations in systems of N electrons (atom or molecule).

   d) How would you describe the exact and an approximate ground state in the H_2 molecule?

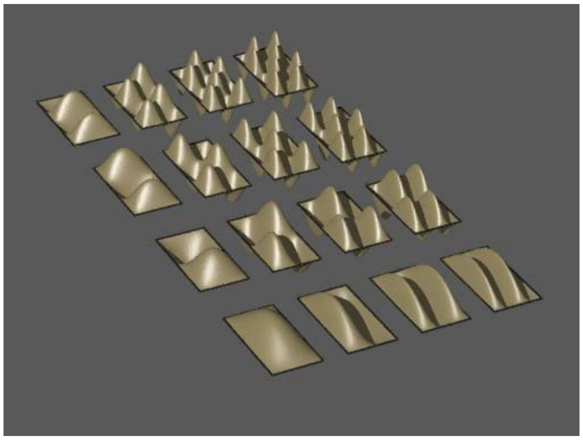
   e) Explain the concept of pure and mixed states in quantum mechanics.

2. a) Try to explain how one can understand the process of thermalization in a subsystem of a larger system that is initially in a pure quantum state.

   b) What is a microstate (illustrate on a system of classical and quantum identical particles)?

   c) How can equilibrium (thermalized) systems of identical particles be described? (consider open and closed systems)

   d) What is a partition function? How would you calculate thermodynamic properties of molecules in a gas phase using quantum mechanics?



(motivation)

Possibly useful formulas:

$e = 1.602 \times 10^{-19}$ C, $h = 6.626\times10^{-34}$ Js, $\varepsilon_0 = 8.854\times10^{-12}$ $J^{-1}C^2m^{-1}$, $c = 2.998\times10^8$ ms^{-1},
$m_e = 9.109 \times 10^{-31}$ kg, , $k_B = 1.38\times10^{-23}$ J K^{-1}.

$$i\hbar\frac{\partial}{\partial t}\Psi(x,y,z,t) = H\,\Psi(x,y,z,t) = \frac{-\hbar^2}{2m}\Delta\,\Psi(x,y,z,t) + U(x,y,z)\,\Psi(x,y,z,t),$$

$$\left\{-\frac{\hbar^2}{2\mu_{AB}}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right] + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right] + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right) + V(r,\theta,\varphi)\right\}\psi(r,\theta,\varphi) = E\,\psi(r,\theta,\varphi),$$

$$k_n\,a = n\,\pi \quad n = 1, 2, 3, 4, \ldots, \quad k_n^2 = \left(\frac{n\,\pi}{a}\right)^2 = \frac{2m\,E_n}{\hbar^2}, \quad E_n = \frac{n^2h^2}{8\,m\,a^2}$$

$$\psi_n(x) = C_1\sin\left(\frac{n\,\pi\,x}{a}\right),\ \langle\psi_n\,|\,\psi_n\rangle = |C_1|^2\int_0^a \sin^2\left(\frac{n\,\pi\,x}{a}\right)dx = 1,\ C_1 = \left[\frac{2}{a}\right]^{1/2},$$

$$\langle\psi_n\,|\,\psi_m\rangle = \delta_{nm}$$

$$p_\theta = \frac{nh}{2\pi}, \quad a_0 = 5.29175\times10^{-11}\,\mathrm{m}$$

$$E_n^{(1)} = \left\langle\psi_n^{(0)}\middle|H'\middle|\psi_n^{(0)}\right\rangle,$$

$$\psi_n^{(1)} = \sum_{m\neq n}\frac{\left\langle\psi_m^{(0)}\middle|H'\middle|\psi_n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}}\psi_m^{(0)},$$

$$H_r = -\frac{\hbar^2}{2\mu_{AB}r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right] + \frac{\mathbf{L}^2}{2I} + V(r,\theta,\varphi),$$

$$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).$$

$$H_r = \frac{\mathbf{L}^2}{2I}, \quad \mathbf{L}^2\,Y_J^M(\theta,\varphi) = \left(L_x^2 + L_y^2 + L_z^2\right)Y_J^M(\theta,\varphi) = \hbar^2J(J+1)\,Y_J^M(\theta,\varphi).$$

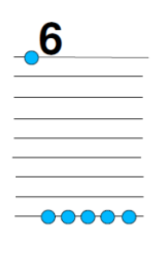
$$[M_x, M_y] = i\hbar M_z, \quad M_+ = M_x + i\,M_y,$$

$$\varphi = a_1\,\chi_1 + a_2\,\chi_2,$$
$$a_1\left[H_{11} - E_\varphi S_{11}\right] + a_2\left[H_{12} - E_\varphi S_{12}\right] = 0,$$
$$a_1\left[H_{21} - E_\varphi S_{21}\right] + a_2\left[H_{22} - E_\varphi S_{22}\right] = 0,$$

$$\hat{1} = \sum_i P_i = (\text{H atom}) = \sum_{nlm}|nlm\rangle\langle nlm| + \int dE\sum_{lm}|Elm\rangle\langle Elm|, \quad \hat{1}\,|\psi\rangle = |\psi\rangle$$

$$\hat{\rho}_T(t) = |\Psi_T(t)\rangle\langle\Psi_T(t)| = \sum_{i,j}c_ic_j^*\left|\psi_{S_i}\right\rangle\left|\psi_{R_i}\right\rangle\left\langle\psi_{R_j}\right|\left\langle\psi_{S_j}\right|, \quad \hat{\rho}_S(t) = \mathrm{Tr}_R\{\hat{\rho}_T(t)\},$$

$$i\hbar\frac{\partial}{\partial t}\rho = [H,\rho], \quad \hat{\rho} = \sum_n\frac{\exp(-\beta\,E_n)}{Z}|E_n\rangle\langle E_n|$$



$$U = \langle E\rangle = \sum_{\alpha=1}^{n^D}P_\alpha\,E_\alpha. \quad Z(T,V,N) = \frac{z(T,V,N)^N}{N!},$$

$$\varepsilon_{int} \approx \varepsilon_{el} + \varepsilon_{vib} + \varepsilon_{rot}, \quad z_{int} = z_{el}\,z_{vib}\,z_{rot}.$$