

Graded problems (total = 100 points)

1. **Atoms in electric fields:** if we apply an electric field \vec{E} to an atom, the electronic cloud will polarize in response to the perturbation, and the atom will acquire an induced electrical dipole. From electrostatics we know that the field is derived from the gradient of the potential: $\vec{E}(\vec{r}) = -\nabla\Phi(\vec{r})$. Suppose now that we have a constant field in the z direction $\vec{E}(\vec{r}) = (0, 0, E_z)$; then the potential is $\Phi(\vec{r}) = -zE_z$. The potential energy is given by the product of the electronic charge (-1 in atomic units) times the potential, i.e. $V = zE_z$. This V is the new term that we need to add to the Hamiltonian to take into account this additional, constant electric field. The other terms in the Hamiltonian will be, using atomic units, the quantum kinetic energy $-\frac{1}{2}\nabla^2$ and the Coulomb potential energy $-\frac{1}{r}$.

$$\left(\hbar = m_{electron} = e \text{ (electronic charge)} = a_0 \text{ (Bohr radius)} = \frac{1}{4\pi\epsilon_0} \text{ (}\epsilon_0 \text{ is the dielectric constant)} = 1 \right)$$

- a. **(35 points):** Find the variational ground-state energy for an electron in a hydrogen atom under a constant applied electric field $\vec{E}(\vec{r}) = (0, 0, E_z)$, using as the a trial wavefunction $A \exp(-\alpha r)$. **Comment and compare** the result with the case of no electric field. (Hint: express the additional potential energy due to the constant field in spherical coordinates; also, remember that when performing integrals in spherical coordinates you need to take into account the change of coordinates:

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz f(x, y, z) = \int_0^{\infty} r^2 dr \int_0^{\pi} \sin \vartheta d\vartheta \int_0^{2\pi} d\phi f(r, \vartheta, \phi). \text{ Even better, just remember}$$

that the integral of an even function times an odd function over a symmetric interval is zero. All other integrals have been explicitly given in class.

- b. **(15 points):** Use now as a trial wavefunction a linear combination of eigenfunctions:

$$A \left(\frac{1}{\sqrt{\pi}} \exp(-r) + c \frac{1}{4\sqrt{2\pi}} r \exp\left(-\frac{r}{2}\right) \cos \vartheta \right) = A (|\psi_{100}\rangle + c |\psi_{210}\rangle). \text{ These are the two}$$

hydrogen eigenfunctions for (n,l,m) equal to (1,0,0) and (2,1,0), whose relative weight is determined by the coefficient c, single parameter in the variational expression for the energy. If you are not familiar with Macsyma/Mathematica/Maple, use

$$\langle \psi_{210} | r \cos \vartheta | \psi_{210} \rangle = 0 \text{ and } \langle \psi_{100} | r \cos \vartheta | \psi_{210} \rangle = \frac{256}{243\sqrt{2}}, \text{ and remember that the}$$

unperturbed Hamiltonian applied to $|\psi_{100}\rangle$ or $|\psi_{210}\rangle$ will give $-\frac{1}{2}|\psi_{100}\rangle$ and $-\frac{1}{8}|\psi_{210}\rangle$ (in atomic units, the ground state energy of the electron in the hydrogen atom is $-0.5 = -0.5 \text{ Hartree} = -1 \text{ Rydberg} = -13.6058 \text{ eV}$). Just arrive at the expression $E(c)$, and comment on why there exists now a minimum for the energy.

2. **(50 points) Statistical mechanics + quantum mechanics explains the ideal gas.** In bonding, we've seen that the solution to the Schrödinger equation for a particle in a three-dimensional box has allowed energy eigenvalues given by:

$$E(n_x, n_y, n_z) = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

Where the dimensions of the box are a , b , and c in the x , y , and z directions, respectively.

- a. If we assume that atoms of an ideal gas in a container are quantum mechanical particles, show that the partition function for a molecule of the ideal gas is:

$$q = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V$$

Hint: Use the approximation that the sums over the 3 quantum numbers in the partition function can be replaced by an integral (valid because the energy levels are very close together at high energies)- the integrals can be evaluated explicitly.

- b. Calculate the total internal energy of an ideal gas (in Joules) from the partition function.

- c. Using $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$ and the ideal gas molecule partition function, derive the ideal gas law $PV = nRT$. (*Hint:* Since an ideal gas is a collection of indistinguishable particles, you may need to use Stirling's approximation: $n! \approx \left(\frac{n}{e}\right)^n$).

- d. Using the following relationship for the chemical potential:

$$\mu_i = -kT \left(\frac{\partial \ln Q}{\partial N_i} \right)_{T,V,N_{j \neq i}}$$

... and the ideal gas law derived above, show that the chemical potential of the ideal gas is the expression we have used in classical thermodynamics calculations:

$$\mu_i = kT \ln \frac{P_i}{P_{i,o}}$$

Where the units of the chemical potential are (J/molecule) and the standard state pressure is given by:

$$P_{i,o} = kT \left(\frac{2\pi mkT}{h^2} \right)^{3/2}$$

Optional non-graded problems:

3. **Atomic polarizabilities:** If we choose the origin of the coordinates to coincide with the nucleus, the induced dipole $\vec{\mu}$ will be given by $-\int \vec{r} \|\psi(\vec{r})\|^2 d\vec{r}$ (the minus sign is due to the fact that we are looking at the electronic charge density). The polarizability α is given by the ratio of the induced dipole vs. the electric field: $\alpha_{ij} = \frac{\mu_i}{E_j}$ (for hydrogen in the ground state,

the induced dipole will be collinear with the field – in our case only E_z and thus μ_z are different from zero, and the polarizability is a scalar quantity, and not a tensor). μ_z is given by $-\int z \rho_{el}(\vec{r}) d\vec{r}$, while μ_x and μ_y are zero due to the cylindrical symmetry along the z-axis of the polarized charge density (the integrals $\int x \rho_{el}(\vec{r}) d\vec{r}$ and $\int y \rho_{el}(\vec{r}) d\vec{r}$ must be zero by symmetry). Find the polarizability of hydrogen using the trial wavefunction of problem 1(a), and eventually for problem 1(b) (in the last case, calculate with a symbolic algebra program

$$\lim_{E \rightarrow 0} \frac{\mu(E)}{E} = \left. \frac{d\mu(E)}{dE} \right|_{E=0})$$

4. **Computing the Boltzmann distribution.** You have a thermodynamic system with three states. You observe the probabilities of these states are $p_1 = 0.9$, $p_2 = 0.09$, and $p_3 = 0.01$ at $T = 300\text{K}$. What are the energies E_2 and E_3 of states 2 and 3 relative to the ground state E_1 ? (i.e., can you determine the ratio E_2/E_1 and E_3/E_1 ?)
5. **The properties of a two-state system.** Suppose a molecule has only 2 energy levels, one with energy 600 J/mole, and one with energy of 1800 J/mole. The molecule can reside in only one of these energy states at any instant. At $T = 300\text{K}$, calculate:
- The partition function, q .
 - The average energy for the molecule, $\langle E \rangle$.
6. **The two-state system redux.** Let's consider a system where each atom can be either in a ground state with energy zero or an excited state with energy ε_0 . The atoms are *identical but indistinguishable*. If the system is comprised of N atoms, then the number of unique states for the system is given by:

$$W(n) = \frac{N!}{n!(N-n)!}$$

Where n is the number of atoms in the excited energy level for a given microstate (This is the statistics of coin flips- two possible outcomes for each atom, either in the ground state or the excited state).

- What is the total energy of the system as a function of n ?
- Derive an expression for the entropy of the system as a function of E , using Stirling's approximation. Make a plot of S vs. E : What can you say about the temperature of this system as its total energy increases?

7. **Chemical potential from the 'stat mech' point of view.** Like all other thermodynamic quantities, the chemical potential can be determined from the partition function. Show that the chemical potential can be written as:

$$\mu_i = -kT \left(\frac{\partial \ln Q}{\partial N_i} \right)_{T, V, N_{j \neq i}}$$

Where the units on the chemical potential are Joules per atom/molecule.

8. **The Ising model of magnetization in materials.** The spins of atoms act like small magnets; magnetic dipoles which can be aligned in a magnetic field to provide a net magnetization to a material (e.g. iron). Below a certain critical temperature, they have a net magnetic moment, but above this temperature the magnetization is erased. E. Ising developed a model to describe this phenomenon by modeling a ferromagnetic crystal as a 1D lattice of magnetic spins as his PhD thesis in 1925 (...a lot of Nobel Prizes were born around this time)- see the figure below.



In this model, a single spin of the system has an energy of zero, whether it is 'up' or 'down'. However, an additional energy is introduced: if two magnetic spins which are nearest neighbors

are aligned in the same direction, either both up or both down, the system gains an additional energy J_0 . If two neighboring spins are oppositely oriented, the system has an additional energy $-J_0$. The spins are considered to be identical but distinguishable (i.e. have defined lattice locations in space).



$$\frac{E_{total}}{kT} = 0 + 0 + J$$



$$\frac{E_{total}}{kT} = 0 + 0 - J$$

- a. Derive the partition function for a 1D chain of N magnetic spins (you too could earn the Nobel prize!). A useful relationship is: $\cosh x = \frac{e^x + e^{-x}}{2}$. Use the shorthand $J = J_0/kT$ and $-J = -J_0/kT$. A good way to solve this problem is to consider first the partition function of one spin alone, then two spins, and so on; identify the pattern that develops as you add more spins to find the expression for an arbitrary large number of spins.
- b. Calculate the heat capacity of the Ising model, and plot it vs. T .