Physics 195 **Problem Set 9** **Due: Tuesday, December 2, 2003**

Problem 1 (Problem 1 from Chapter 19 of Ashcroft and Mermin, page 393). Origin of the van der Waals Force

Consider two noble gas atoms a distance R apart, represented by fixed nuclei of charge Ze located at 0 and R, each surrounded by Z electrons. The electrons bound to the nucleus at 0 have coordinates $r_i^{(1)}$ and those bound to the nucleus at R have coordinates $r_i^{(2)}, i = 1, ..., Z$. We suppose R to be so large that there is negligible overlap between the electronic charge distributions about the two nuclei. [22] Let H_1 and H_2 be the Hamiltonians for atoms 1 and 2 alone. The Hamiltonian for the two-atom system will be $H = H_1 + H_2 + U$, where U gives the Coulomb interaction between all pairs of charged particles, one from atom 1, and one from atom 2:

$$U = e^2 \left[\frac{Z^2}{R} - \sum_{i=1}^{Z} \left(\frac{Z}{|R - r_1^{(1)}|} + \frac{Z}{r_i^{(2)}} \right) + \sum_{i,j=1}^{Z} \frac{1}{|r_i^{(1)} - r_j^{(2)}|} \right] . \quad \mathbf{(19.5)}$$

To second order in perturbation theory, the interaction energy between the two atoms will be given by:

$$\Delta E = \langle 0|U|0\rangle + \sum_n \frac{|\langle 0|U|n\rangle|^2}{E_0 - E_n}, \quad \mathbf{(19.6)}$$

where $|0\rangle$ is the ground state of the unperturbed two-atom system, and $|n\rangle$ its excited states.

(a) Show that the first-order term in (19.6) is just the electrostatic interaction energy between two distributions of charge density $\rho^{(1)}(r)$ and $\rho^{(2)}(r)$, where $\rho^{(1)}$ and $\rho^{(2)}$ are the ground-state charge distributions of atoms 1 and 2.

(b) Prove that if the charge distribution have zero overlap and are spherically symmetric, this interaction energy is identically zero.[23]

(c) The assumption that there is negligible overlap between the electronic states on the two atoms also means that the wave functions appearing in the second order term in (19.6) are negligibly small unless $|r_i^{(1)}|$ and $|r_i^{(2)} - R|$ are small compared with R. Show that if (19.5) is expanded in these quantities, the leading nonvanishing term is

$$\frac{-e^2}{R^3} \sum_{i,j} \left[3(r_i^{(1)} \cdot \hat{R})([r_j^{(2)} - R] \cdot \hat{R}) - r_i^{(1)} \cdot (r_j^{(2)} - R) \right] . \quad \mathbf{(19.7)}$$

(d) Show, as a result, that the leading term in (19.6) varies as $1/R^6$ and is negative.

Problem 2(Problem 4 from Chapter 20 of Ashcroft and Mermin, page 413).

(a) As a very crude model of an alkali metal, suppose that the charge of each valence electron is uniformly distributed through a sphere of radius r_s about each ion. Show that the electrostatic energy per electron is then

$$u^{coul} = -\frac{9a_0}{5r_s}\text{Ry/electron} = -\frac{24.49}{(r_s/a_0)}\ \text{eV/electron.} \quad (\mathbf{20.34})$$

(This is remarkably close to the result (20.24) for a bcc lattice of ions immersed in a completely uniform distribution of compensating negative charge.)

(b) In a real metal the valence electrons are largely excluded from the ion core. If we take this into account by uniformly distributing the charge of each electron in the region between spheres of radius r_c and r_s about each ion, and then replacing the potential of each ion by the pseudopotential,

$$V_{ps}(r) = \frac{-e^2}{r}, \quad r > r_c$$

$$= 0, \quad r < r_c, \quad (\mathbf{20.35})$$

show that (20.34) must be replaced to leading order in r_c/r_s by

$$\frac{-9a_0}{5r_s} + \frac{3(r_c/a_0)^2}{(r_s/a_0)^3}\text{Ry/electron.} \quad (\mathbf{20.36})$$

(c) Taking the energy per particle to be the sum of the kinetic (20.25), exchange (20.26), and potential (20.36) energies, show that the equilibrium value of r_s/a_0 is given by

$$r_s/a_0 = 0.82 + 1.82(r_c/a_0)[1 + O(a_0/r_c)^2], \quad (\mathbf{20.37})$$

and compare this with the values given in Table 1.1 and Table 19.4.