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TITLE: A SELF-CONSISTENT FIELD MODEL FOR CONDENSED MATTER

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A self-consistent field model for condensed matter[†]

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Abstract. A model for condensed matter is described in which the ions surrounding a particular atom are replaced by a constant density positive charge background outside of a spherical cavity. Electrons provide sufficient negative charge to neutralize the atomic nucleus at the center of the cavity and the positive charge outside. The orbital functions of the electrons, both bound and free, are obtained as solutions of the Dirac equation and are used to self-consistently determine the potential function. A prescription is given for separating the total volume and the total free energy of the system into parts associated with the atom and the surrounding medium.

The Wigner-Seitz sphere radius at which the atomic free energy is lowest has been found for each of 14 elements including the 5d transition metals. They differ from the sphere radii based on measured densities by from 2 to 8 per cent. It is expected that results will improve in the high pressure region for which this model is mainly intended.

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Electronic structure calculations for solids are much more difficult than the equivalent ones for atoms. This stems largely from the loss of spherical symmetry that goes with a periodic array of atoms. Many attempts have been made to restore spherical symmetry to the electronic structure problem for condensed matter. Some have had a fair degree of success; others have contained unwarranted assumptions which led to poor results. This paper is a brief description of another attempt in this direction. It is similar in many respects to some recent work of Almbladh and von Barth (1976) but has significant differences as well.

The main motivation has been the desire to study the bulk properties of highly compressed matter. The valence electrons in a highly compressed solid will have large kinetic energies and, as a result, a free-electron-like character in parts of the atomic cell where the potential is weak. This suggests that a compressed atom in a solid (or liquid) could be "taken out" and then imbedded in a uniform electron gas of appropriate density without much change in electronic structure. This is the idea behind the simple model illustrated in Fig. 1. A nucleus of charge Ze is supposed to be at the center of a spherical cavity of radius R . Outside the cavity there is more positive charge (with a constant density $\bar{\rho}_e$) which is supposed to represent the ions surrounding the atom at the center of the cavity. And then there are enough electrons to neutralize all of the positive charge. In this model the cavity radius R is chosen so that the electronic charge inside neutralizes the nuclear charge, and the electronic charge outside is sufficient to neutralize the uniformly distributed positive charge outside.

The model has been developed in the self-consistent field approximation in a manner essentially the same as in ordinary atomic calculations.

The main difference is that, in addition to bound electrons, there are electrons in continuum states which contribute to the charge density and other physical quantities. The local density approximation for exchange has been used (Kohn and Sham 1965). Relativistic effects have been included through the use of the Dirac equation since we are interested in the heavier elements. Also thermal effects have been included in a mean field approximation. A mathematical formulation has been given through a free energy functional which is minimized subject to appropriate constraints. From this minimization are obtained the one-electron wave equations and the potential function, the cavity radius, the chemical potential, and the average occupations of the one-particle states.

One problem remains in completing this model of condensed matter. The atom being considered is part of a very much larger system. But what we are interested in are the physical quantities that belong to the atom alone: its volume, energy, entropy, etc. We want to separate each of these into a part belonging to the atom and a part associated with the surrounding electron gas. There is no unique way of doing this, so we have settled for the following somewhat arbitrary prescription. The total volume is written as $V = V_0 + \Delta V$ where ΔV , the volume of the atom, is given. The total number of electrons is the sum of the average occupation numbers for the one-electron states:

$$N = \sum_i n_i = \sum_b n_b + \int \frac{d^3k}{(2\pi)^3} 2V n_k + \sum_{j\ell} (2j+1) \int \frac{dk}{\pi} \frac{d\delta_{j\ell}}{dk} n_k .$$

The index b indicates the bound states and k the continuum states. The last term on the right is a Friedel sum (Landau and Lifshitz 1959).

We can put $V = V_0 + \Delta V$ in the second term on the right and then regard the integral containing V_0 as the number of electrons in the electron gas which surrounds the atom. This is subtracted from N and there remains

$$\Delta N = \sum_b n_b + \int \frac{d^3 k}{(2\pi)^3} 2\Delta V n_k + \sum_{j\ell} (2j + 1) \int \frac{dk}{\pi} \frac{d\delta_{j\ell}}{dk} n_k$$

which is the number of electrons associated with the atom and which must equal the nuclear charge, Z . The chemical potential appearing in the average occupation factors, n_i , is adjusted to meet this requirement. The free energy and entropy per atom are determined in much the same way, and the pressure is obtained by numerically differentiating the free energy along an isotherm. It is worth remarking that the volume of the cavity is not the same as ΔV which appears in the equation above, although they are usually within a few per cent of each other.

It is expected that this model will be at its best when the valence electrons are free-electron-like in character. It is interesting to see how well it will work for solids which are not of this type such as the transition metals. We have chosen the 5d series since less electronic structure work has been done on this group of metals than on the others and since we are able to account for relativistic effects. In Fig. 2 are shown calculated and experimental Wigner-Seitz sphere radii at zero pressure. (The calculations were done for a temperature of 0.2 eV which for present purposes is close to zero.) While not as good as the self-consistent field band structure results obtained by Moruzzi, Williams and Janak (1977) for the 3d and 4d transition metals, they are still reasonable. As might be expected, the metals which are most free-electron-like are described best by this model.

We feel that this model may be useful in many theoretical studies in condensed matter physics besides those for which it is designed. It produces charge densities and potential functions appropriate to an atom closely surrounded by other atoms. Orbital functions, both bound and continuum, may be obtained. Phase shifts for the continuum states are calculated. Since the model is fairly simple it may be used to test such things as the importance of relativistic effects or the merits of different prescriptions for exchange and correlation contributions to the potential function.

We hope to publish a fuller description of the model, its mathematical development, and the computer program used for the calculations at some later date.

References

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Figure Captions

Figure 1. . A schematic distribution of charge for this model: A -- a point nucleus at the center of a spherical cavity; B -- a constant positive charge density outside the cavity which represents the surrounding ions; C -- a spherically symmetric electronic charge density inside the cavity; D -- a volume averaged electronic charge density outside the cavity. R is the radius of the cavity which is electrically neutral. The outside region is also neutral.

Figure 2. Calculated and measured Wigner-Seitz sphere radii for the 5d transition metals and some other elements in the same row of the periodic table.