Correction of the statistical model of matter near nuclei

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Refined quantum corrections are derived for the energy and pressure of "cold matter" near a nucleus, where the semiclassical approximation breaks down. These corrections are not negligible. For an isolated atom they yield the Scott correction. They disappear in the high-compression limit in a manner consistent with an exact quantum-mechanical calculation.

The semiclassical condition which underlies the Thomas–Fermi (TF) model is violated close to a nucleus, at $r<r_0$, where r_0 has the values Z^{-1} and $(Z/n)^{1/2}$ (in atomic units) in the respective regions

$$n \ll Z^3 \ (\mathrm{A}), \quad n \gg Z^3 \ (\mathrm{B}), \tag{1}$$

where $Z \gg 1$ is the atomic number, and n is the electron density. The energy corresponding to the TF model may therefore by quite different from the exact value. For the same reason, the quantum corrections which are introduced to reduce this discrepancy (a) diverge at the point $r=0$ and (b) have a nonvanishing finite part, in contradiction of perturbation theory, in region (1B). Similar difficulties exist in the "hot" case, which will be discussed separately. Several methods for overcoming difficulties (a) have been described in the literature.[1–7] For example, incorporating the exact Coulomb expressions for the energy of deep levels of an uncompressed atom, which correspond to motion in the region $r<r_0$, where

$$U \simeq -z/r \tag{2}$$

(U is the self-consistent field), leads to an effective cutoff of the divergences at a distance r_0 and to a replacement of these divergences by the Scott correction $E_{\mathrm{Sc}}=Z^2/2$ (Refs. 1–4).

In this letter we discuss a general approach, i.e., one which eliminates the two difficulties, (a) and (b), in a common way. This approach leads to an expression for a refined (specified by a superscript c) quantum correction to the energy of the lower (second) order (the subscript 2):

$$\delta_2 E^c = \frac{2}{9} E_{\mathrm{ex}} + E_{\mathrm{Sc}} + \Delta, \tag{3}$$

where E_{ex} is the exchange correction,[8] and the quantity Δ [see Eq. (11) below] is such that expression (3) has the necessary properties.

1. We introduce the difference δA between the quantum-mechanical value of A (in the Hartree approximation) and the value corresponding to the TF model. For the energy of the system, this difference is[8]

$$\delta E=-\int_{-\infty}^{\mu} d\mu'\delta N(\mu')=-2\int_{-\infty}^{\mu} d\mu'(\mu-\mu')\delta\rho(\mu'), \tag{4}$$

where N is the total number of particles, ρ is the density of levels,

$$N=2\int_{-\infty}^{\mu} d\mu'\rho(\mu'), \quad \rho(\mu)=\mathrm{tr}\delta(\mu-\hat{H}), \quad \hat{H}=\hat{p}^2/2+U(\mathrm{x}),$$

$$\delta\rho(\mu)=-\frac{1}{\pi}\,\mathrm{Im}\int d\mathrm{x}G(\mathrm{x},\mathrm{x}|\mu)-\int d\mathrm{x}p_0(\mathrm{x})/2\pi^2, \tag{5}$$

G is a retarded Green's function, and $p_0=[2(\mu-U)]^{1/2}$ is the Fermi momentum.

For a positive chemical potential it is convenient to replace (4) by the expression (here and below, $M\to\infty$)

$$\delta E=\frac{Z^2}{4}+2\int_{\mu}^{M} d\mu'(\mu-\mu')\delta\rho(\mu'), \tag{6}$$

which results from sum rules derived from (5):

$$\int_{-\infty}^{\infty} d\mu'\delta\rho(\mu')=0, \qquad \int_{-\infty}^{M} d\mu'\mu'\delta\rho(\mu')=\frac{Z^2}{8}.$$

2. In second order in the gradients we find[9]

$$\delta_2\rho(\mu)=\frac{1}{192\pi^2}\frac{\partial^2}{\partial\mu^2}\int dx\left[4p_0\Delta p_0^2+\frac{(\nabla p_0^2)^2}{p_0}\right].$$

The TF equation

$$\Delta p_0^2=\frac{8}{3\pi}p_0^3-8\pi Z\delta(\mathrm{x}) \tag{7}$$

and the equality $(\nabla p_0^2)^2/2p_0=\nabla(p_0\nabla p_0^2)-p_0\Delta p_0^2$ make it possible to separate from (6) some divergences (denoted below by inf) which are generated by a singularity of the Coulomb interaction at the point $r=0$:

$$\delta_2 E=\frac{2}{9}E_{\mathrm{ex}}+\frac{Z^2}{4}+\mathrm{inf}, \tag{8}$$

where

$$E_{\mathrm{ex}}=-\frac{1}{4\pi^3}\int d\mathrm{x}p_0^4$$

is the exchange correction.

3. To eliminate the difficulties inherent in (8), we use relation (2) and the fact that an exact solution of the problem is known for the case of a Coulomb field. The refined expression for $\delta_2 E$ is written in the form

$$\delta_2 E^c = \delta_2 E - \delta_2 \tilde{E} + \delta \tilde{E}, \tag{9}$$

where the tilde (~) corresponds to an auxiliary system with the same value of μ, whose electrons interact only with the nucleus ($U = -Z/r$ for all r). We restrict the discussion below to the case of a nonnegative chemical potential μ. The discrete spectrum then does not contribute in the auxiliary system according to (6); i.e., there are no shell corrections. The contributions of the first two terms on the right side of (9) in the region $r < r_0$, in which (2) holds, cancel out, and we are left with the exact solution of the Coulomb problem. In the region $r > r_0$, on the other hand, where the motion is semiclassical, the contributions of the last two terms in (9) cancel out, and we are left with the original quantum correction.

Proceeding as in Sec. 2, but noting that the first term on the right side of (6) is absent, and thus using the inequality $\int d\mathrm{x} \Delta p_0^2 = -8\pi Z \neq 0$, we find

$$\delta_2 \tilde{E} = \frac{Z}{6\pi} (\sqrt{2\mu} - \sqrt{2M}) + \frac{Z^2}{4} + \mathrm{inf}. \tag{10}$$

Since the quantity inf here is the same as in (8), it drops out of the result.

4. Equations (5) and (6) and the expression for the Coulomb Green's function,[11]

$$G(\mathrm{x}, \mathrm{x}' | \mu) = \frac{ik}{2\pi} \int_1^\infty ds \exp(i\alpha) J_0(\beta),$$

$$k = \sqrt{2\mu}, \quad \alpha = k(r+r')s + \frac{Z}{k} \ln \frac{s+1}{s-1}, \quad \beta = k[2(rr' + \mathrm{xx}')(s^2-1)]^{1/2},$$

$$r = |\mathrm{x}|, \quad r' = |\mathrm{x}'|,$$

lead to the relation

$$\delta \tilde{E} = E_{\mathrm{Sc}} + \frac{Z}{6\pi} (\sqrt{2\mu} - \sqrt{2M}) + \frac{Z^2}{\pi} f(\sigma), \tag{11}$$

where $\sigma = Z/\sqrt{2\mu}$ is the Coulomb parameter of the perturbation theory.

Introducing the expectation value

$$\langle a(y) \rangle_n = \frac{n}{y^n} \int_0^y dx x^{n-1} a(x),$$

we can express $f(\sigma)$ in terms of the gamma function of imaginary argument:

$$f(\sigma) = \mathrm{Im} \langle \ln \Gamma(i\sigma) \rangle_2 - 2\sigma(\ln\sigma - 4/3)/3 + 1/6\sigma + \pi/4.$$

In regions (1A) ($\sigma \gg 1$) and (1B) ($\sigma \ll 1$), the function $f(\sigma)$ has the respective values

$$1/180\sigma^3 + O(1/\sigma^5), \quad 1/6\sigma - \pi/4 + O(\sigma).$$

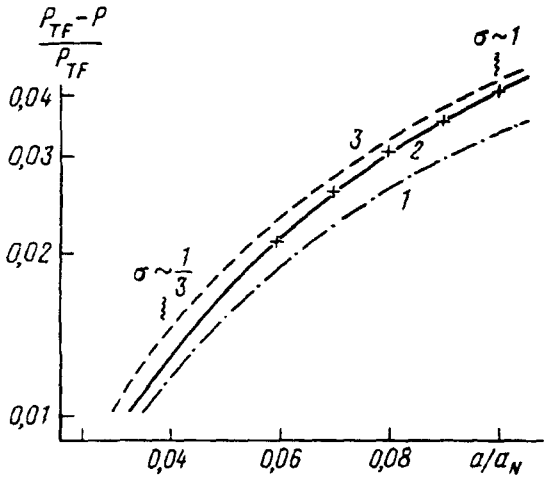

FIG. 1. Comparison of various model equations of state of aluminum. *1*—Thomas–Fermi (TF) model with an exchange correction P_{ex} (perturbation theory); *2*—TF model with an exchange correction and an unrefined quantum correction $\delta_2 P$ (the TFP model); *3*—TF model with an exchange correction and with a refined quantum correction, (13); +—method of augmented plane waves. Here a/a_N is the reduced lattice constant, $a_N=7.65288$, and σ is the Coulomb parameter of the perturbation theory.

5. Substituting (8), (10), and (11) into (9), and comparing it with (3), we find the final expression, which is not afflicted by difficulty (a) (see the discussion at the beginning of this letter):

$$\Delta=\frac{Z^2}{\pi}f(\sigma). \tag{12}$$

In region (1A) the quantity Δ is small, and the result reduces to the sum $\frac{2}{9}E_{ex}+E_{Sc}$ (the same result is valid[1-4] for an uncompressed atom with $\mu=0$). In region (1B), on the other hand, the quantity Δ cancels the quantum correction $\frac{2}{9}E_{ex}$ (the remainder $Z^2/4$ is small in this region), and the energy is, in agreement with perturbation theory, equal to the sum of the kinetic component, the Madelung component, and the exchange component.[8]

A topic of direct interest is the refined correction to the pressure $P=-\partial E/\partial V$. We write an explicit expression for this correction for the region $n\gg Z^2$, where the electron gas is essentially uniform, and where we have

$$p_0=(3\pi^2 n)^{1/3},\quad \mu=p_0^2/2,\quad \sigma=Z/p_0.$$

Correlation effects are small in this region, and we can legitimately compare the model of a self-consistent field with the exact solution. Introducing the digamma function $\psi=\Gamma'/\Gamma$, we find

$$\delta_2 P^c=-\frac{2}{27}\frac{Z^4}{\pi^3\sigma^2}\left[\mathrm{Re}\langle\psi(i\sigma)\rangle_3-\ln\sigma+1/3\right]. \tag{13}$$

In region (1A) this quantity reduces to

$$\delta_2 P = \frac{2}{9} P_{ex} = -\frac{Z^4}{54\pi^3\sigma^4},$$

while in region (1B) its contribution can be ignored: $\delta_2 P^c / P_{ex} \sim \sigma^2 \ln\sigma$.

6. We conclude with a look at the transition region between (1A) and (1B). Figure 1 shows the relative deviation from the TF model of the results, calculated for the pressure of aluminum according to various models, as a function of the compression in the region of interest, $n \gg Z^2$. We see a fairly good quantitative agreement between the results of the theory presented above and those of a comprehensive quantum-mechanical calculation by the method of augmented plane waves.[12]

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