Comment on "Core overlap interaction in metals"

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In a recent paper, Benedek has investigated the interatomic forces associated with the overlap of closed shells in metals. For the description of the high core-core interaction case, Benedek has chosen Firsov's formula which is based on the Thomas-Fermi (TF) model of a neutral atom. It is the purpose of the present comment to point out that by making use of variational modifications of the TF theory for atoms and ions, Firsov's formula (a) may be extended beyond the 1-Å internuclear separation range, and (b) may also be applied (with appropriate modifications) for the description of the overlap interaction between ions.

In a recent paper, Benedek[1] has investigated the interatomic forces associated with the overlap of closed shells in metals. Benedek finds that, in metals that have only s and p electrons in their outer closed shells, the core overlap interaction is small at normal lattice separations. On the other hand, Benedek also finds that, for metals with d electrons in their outer closed shells, core overlap at normal lattice separations is quite pronounced. Into this category fall noble metals, containing d electrons in their outermost closed shells, where Benedek finds that core overlap is significant at and around the nearest-neighbor position.

Benedek has also investigated the construction of a composite interatomic potential between low-energy and high-energy theories. This has been done by interpolation. He finds that the core-core interaction is extremely sensitive to the assumed core wave functions or, stated equivalently, to the assumed core electron densities. He attributes to this fact one of the main sources of error in the calculated core-core interaction energies.

For the description of the high core-core interaction case, Benedek has chosen Firsov's formula[2] which is based on the Thomas-Fermi (TF) model of a neutral atom.[3] The case considered by him for metallic Zn covers internuclear separations from 0.1 to 0.7 Å, thus falling into the less than 1-Å range considered as a limit for the validity of Firsov's formula.

It is the purpose of the present note to point out that Firsov's formula may be extended (a) beyond the 1-Å internuclear separation range, and (b) may also be applied to the interaction between ions with appropriate modifications.

(a) The reason for the restriction of Firsov's formula lies in the fact that the original TF model, on which Firsov's formula is based, leads to an atom which is "too big." This has been ascertained by Sommerfeld,[4] who has shown that the radial electron density, in a neutral atom, falls off as

the inverse fourth power of the distance from the atomic nucleus, whereas the Hartree method,[5] the quantum-mechanical equivalent[6] of the TF model, leads to an exponentially decreasing radial electron density.

It has been possible to eliminate[7,8] the "too-big" feature of an atom from the original TF theory by making use of an equivalent variational principle. The improvement on the electron-density distribution of an atom, brought about by the variational principle, lies in the fact that the variational principle permits one to prescribe via which route the solution of the (nonlinear) TF equation should reach zero value at infinity. Calculations of various atomic constants[8,9] have shown that the data obtained by the variationally modified TF model are in better agreement with the experimental values than those obtained with the original TF model. This fact might be looked upon as a confirmation of the realistic nature of the variational solution of the TF equation at all values of the distance from the atomic nucleus.

Firsov's formula, used by Benedek, is of the form

$$U_F = (Z^2 e_0^2 / R) \chi_e(\xi_F), \qquad (1)$$

where Z is the atomic number, e_0 is the magnitude of the electron charge, R is the internuclear separation, and χ_e is the (original numerical) TF function.[10] The quantity ξ_F, in Firsov's theory, is given by

$$\xi_F = (2Z^{1/2})^{2/3} R / C, \qquad (2)$$

where C stands for

$$C = \tfrac{1}{4}(9\pi^2/2)^{1/3} a_B, \qquad (3)$$

and a_B denotes the Bohr radius.

The approximate variational solution of the TF equation for a neutral atom is given[7,8] by

$$\chi_v(\xi) = (a_0 e^{-\alpha_0 \xi} + b_0 e^{-\beta_0 \xi})^2, \qquad (4)$$

where a_0, b_0, α_0, and β_0 are constants, with val-

ues

$$a_0 = 0.721\,833\,7, \quad b_0 = 0.278\,166\,3, \tag{5}$$

$$\alpha_0 = 0.178\,255\,9, \quad \beta_0 = 1.759\,339,$$

and ξ is the dimensionless variable

$$\xi = r/\mu, \tag{6}$$

with

$$\mu = C Z^{-1/3}. \tag{7}$$

(b) As mentioned before, Firsov's formula is only applicable to the interaction of a neutral atom with a neutral atom. Recently it has been possible to obtain an approximate variational solution of the TF equation (without the finite-radius feature of the original theory) for ions,[8] which is of the form

$$\chi_{vi}(\xi) = (a_i e^{-\alpha_i \xi} + b_i e^{-\beta_i \xi})^2, \tag{8}$$

where

$$a_i = a_0 + \Delta a(Z, N), \quad b_i \dot= b_0 + \Delta a(Z, N),$$
$$\alpha_i = \alpha_0 + \Delta\alpha(Z, N), \quad \beta_i = \beta_0 + \Delta\beta(Z, N). \tag{9}$$

In Eq. (9), Z stands for the atomic number, N for the number of electrons in a particular ion, and the quantities prefaced by Δ's are correction quantities (for which detailed expressions are given elsewhere[8]).

Benedek finds that core wave functions are somewhat different in a metallic environment than in isolated atoms. For this reason, arguments can

be advanced whether electron densities in neutral atom cores, or electron densities in ion cores are more suitable for the calculation of the core-core interaction energies.

The advantage of Eq. (8), as seen by this author, lies in the fact that it permits the consideration of the interaction even of "fractionally ionized" atoms since the quantities prefaced by Δ's [in Eq. (9)] are not restricted to integer values of Z and N. A case of fractional ionicity might be quite realistic since, as Benedek states, hybridization involving d electrons makes it somewhat uncertain just how many electrons one should assign to the core of a metal in the lattice. This suggestion merely serves to point out the existence of a tool.

In summary, the present note points out that (a) Firsov's formula for atom-atom interactions can be extended beyond the $R \cong 1$-Å range, and (b) it can also be extended to the interaction of (possibly even fractionally charged) ions.

Finally, it is noted that calculation of interatomic interactions has also been made feasible[11,12] by building charge densities from self-consistent field one-electron wave functions and then considering the interaction of these charge densities. An advantage of these methods over Firsov's method lies in the fact that they also consider the exchange effect. It is, however, pointed out that recently the exchange effect has been (approximately) incorporated into the variationally modified Firsov theory. Within this framework, Eq. (1) is retained but $\chi_e(\xi_F)$ is replaced by $\chi_v(\tilde\xi)$, where

$$\tilde\xi = \frac{12}{7}\left(\frac{2}{9\pi^2}\right)^{1/3}\left[\frac{\phi'_{12}(0)(Z_1+Z_2)^{7/3} - \phi'_1(0)Z_1^{7/3} - \phi'_2(0)Z_2^{7/3}}{\chi'_v(0)Z_1 Z_2}\right]\frac{R}{a_B} + \left[\frac{C_{12}(Z_1+Z_2)^{5/3} - C_1 Z_1^{5/3} - C_2 Z_2^{5/3}}{\chi'_v(0)Z_1 Z_2}\right]\frac{R}{a_B}. \tag{10}$$

In Eq. (10), for the interaction between two neutral atoms, $\phi_{12} = \chi_v(Z_1 + Z_2)$, $\phi_1 = \chi_v(Z_1)$, $\phi_2 = \chi_v(Z_2)$; for that between a neutral atom (Z_1) and an ion (Z_2), $\phi_{12} = \chi_{vi}(Z_1 + Z_2)$, $\phi_1 = \chi_v(Z_1)$, $\phi_2 = \chi_{vi}(Z_2)$; while for that between two ions,

$\phi_{12} = \chi_{vi}(Z_1 + Z_2)$, $\phi_1 = \chi_{vi}(Z_1)$, $\phi_2 = \chi_{vi}(Z_2)$. The quantities C_{12}, C_1, and C_2 are constants, related to definite integrals involving the functions ϕ_{12}, ϕ_1, and ϕ_2, and they are discussed further in Ref. 13.

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