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Immersion of an inert-gas atom or H_2 molecule into jellium: Modified electron-gas approach

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The immersion energy of an inert-gas atom or H_2 molecule into jellium is calculated using an electron-gas approximation. Our modification of the energy functional of Gordon and Kim [J. Chem. Phys. **56**, 3122 (1972)] includes a correction to remove the self-exchange term from the exchange energy and adjustments to take into account the nonuniformity of the system. The calculated ratio of the immersion energy to the jellium density varies about a factor of 2 over five orders of magnitude variation in jellium density and agrees relatively well (within a factor of 2) with the result of previous density-functional approaches in the low-density limit; the Gordon-Kim model is not reliable, however.

The problem of physical (or van der Waals) interactions is currently of great interest. Interatomic interactions are well characterized experimentally in many cases. The analogous problem of physical adsorption is one for which a vast body of information has become available in recent years, but the potentials are somewhat less well known.[1] In both cases, an intense theoretical effort has been undertaken with both *ab initio* and semiempirical techniques. This paper represents an attempt to develop and test the "electron-gas"-type approach first applied some years ago by Gordon and Kim.[2,3] An assessment is made of a newly proposed model and several others by calculating the energy of immersing various atoms or H_2 into jellium. This is a well-defined prototype of the two intended applications mentioned above.

The Gordon-Kim (GK) method was used to evaluate the interaction between two inert-gas atoms from the expressions

$$V=E[n]-E[n_A]-E[n_B]\ , \tag{1}$$

$$E=E_C+E_{\rm EG}\ ,$$

$$E_{\rm EG}[n]\equiv\int d^3r\, n(\mathbf{r})\varepsilon[n(\mathbf{r})]\ . \tag{2}$$

Here E_C is the Coulomb (electrostatic) energy $\varepsilon[n]$ is the energy per particle of the electron system; both are functionals of the total density $n(\mathbf{r})$ and $n_A(\mathbf{r})$ and $n_B(\mathbf{r})$ represent the densities of the isolated atoms A and B. While Eq. (1) is exact in principle (according to density-functional theory[4]), actual practice requires specification of an approximate ε. The original GK effort utilized *local* approximations for the various parts of ε based on the *uniform* electron gas. In atomic units (hartrees and Bohr radii) these are

$$\varepsilon=\varepsilon_k^{(0)}(n)+\varepsilon_{\rm ex}^{(0)}(n)+\varepsilon_{\rm corr}^{(0)}(n)\ , \tag{3}$$

$$\varepsilon_k^{(0)}=\tfrac{3}{10}(3\pi^2)^{2/3}n^{2/3}\ , \tag{4}$$

$$\varepsilon_{\rm ex}^{(0)}=-\frac{3}{4}\left[\frac{3}{\pi}\right]^{1/3}n^{1/3}\ . \tag{5}$$

The subscripts in Eq. (3) refer, respectively, to the kinetic, exchange, and correlation energies of the electron gas; an interpolation formula was used for the last term. An additional assumption in the GK approach is to assume additivity of charge

$$n(\mathbf{r})=n_A(\mathbf{r})+n_B(\mathbf{r})\ . \tag{6}$$

If valid, this implies that the charge rearrangement energy due to proximity of atoms A and B is negligible. Indeed, Heller *et al.*[5] justified this in part by showing that the extra interaction energy due to the difference between the true density and the simply added density, say, $\Delta(\mathbf{r})$, is of the order of $\Delta(\mathbf{r})^2$.

The potential value of the GK method stems from the simplicity of Eq. (6), which by fiat eliminates the problem of self-consistency. However, the method has been shown to have fairly serious flaws[3,6-9]; as a consequence alternative models have been presented and investigated.[3,6-9] We develop here one such variant.

Rae[6] pointed out that a correction is required to remove the self-exchange term from $\varepsilon_{\rm ex}$; this introduces a correction factor

$$\gamma(N)=1-4\beta/3+\beta^2/2-\beta^4/48\ , \tag{7}$$

where β is the solution of a nonlinear equation involving the number of electrons N.[6] Lloyd and Pugh[7] argued that N should include only the valence electrons; Clugston and Pyper[10] confirmed this empirically by comparing the results with Hartree-Fock interatomic potentials. Wood and Pyper[11] found similar behavior in the assumed context of the validity of Eq. 6.

Another issue is correlation; at large separation this is responsible for the asymptotic power-law dispersion energy ($\propto r^{-6}$). The local GK approximation yields instead an exponential dependence for large r because the energy terms are all proportional to powers of n. In this connection, one notes that a spurious attractive well arises in the GK theory without correlation.[12] This is due to an underestimate of the kinetic energy associated with the local approximation. Waldman and Gordon[8] suggested an empirical procedure to correct for this: simply multiply the individual energy terms in (3) by correction factors derived from Hartree-Fock (HF) calculations for the individual atoms. Le Sar[9] modified this in an empirical way suggested by the results for Ne.

Our approach has been guided by these efforts and by a recent paper of Lee and Parr;[13] the latter developed a "Gaussian" hypothesis for the single-particle density matrix which leads to modified coefficients in the energy terms (4) and (5). Our assumed energy functions are

$$\varepsilon_k = S_k \varepsilon_k^{(0)} , \tag{8}$$

$$\varepsilon_{\mathrm{ex}} = S_{\mathrm{ex}} \varepsilon_{\mathrm{ex}}^{(0)} , \tag{9}$$

$$S_k = K_{\mathrm{HF}} / K_{\mathrm{EG}} , \tag{10}$$

$$S_{\mathrm{ex}} = \gamma X_{\mathrm{HF}} / X_{\mathrm{EG}} , \tag{11}$$

where the S_k correction factor is the Hartree-Fock kinetic energy relative to the electron-gas expression for an atom; the X ratio is a similar ratio for exchange. Numerical values for atoms have been taken from Refs. 13 and 14. In the case of H_2 electron-density results were obtained from Refs. 15 and 16. γ in Eq. (11) represents the self-energy correction factor. In our application to the immersion problem, we modified Lloyd and Pugh's correction factor[7] for molecular systems, γ_{LP}, because one component of the system (jellium) is infinitely extended while the other (immersed atom) is finite. We simply take the geometric mean rule, i.e.,

$$\gamma = (\gamma_{\mathrm{atom-atom}} \gamma_{\mathrm{jellium-jellium}})^{1/2} = \gamma_{\mathrm{atom-atom}}^{1/2} = \gamma_{\mathrm{LP}}^{1/2} , \tag{12}$$

where $\gamma_{\mathrm{jellium-jellium}} = 1$. Table I presents our correction factors and those of other workers.

The immersion problem has received attention recently because of the application of effective medium theory to physical adsorption.[17-20] While the latter involves a nonuniform electron gas at a surface, the infinite jellium model is a simpler prototype which provides a testable reference. Given a rigid positive background of constant density n and a dynamic electron gas of the same average density, one determines the energy E of immersing an inert-gas atom. For small n, it has been found that E is proportional to n:

$$E \to \alpha n \quad (n \to 0) , \tag{13}$$

where α has been computed using numerical density-functional methods[17,20,21] or analytically,[22] in terms of the diamagnetic susceptibility and a modified scattering length.[23] The various results for α agree within $\sim 20\%$. Figures 1–4 present results of

$$\alpha(n) \equiv E(n)/n \tag{14}$$

for the atoms He, Ne, and Ar, and the H_2 molecule computed for the immersion problem by evaluating Eq. (1) with Eqs. (8) and (9). We observe in all cases that the method works relatively well, agreeing typically within a factor of 2 with the value calculated at low n. The calculations yield a n dependence of α which is small, about a factor of 2 over five orders of magnitude variation in n.

The regime of relevance to interatomic interactions and physical adsorption is $n \sim 10^{-4}$–10^{-5} a.u. (Refs. 19, 24, and 25). At this density, the assumption of a weakly perturbed atom should be satisfied; thus near constancy of α is expected at least up to this n value. We may determine E by a Taylor-series expansion of the energy functional [Eq. (2)] in density in the limit of $n \to 0$;

$$\begin{aligned} E &\to n \int d\mathbf{r} \left[\frac{\partial \varepsilon_G(\rho)}{\partial \rho} \right], \quad n \to 0 \\ \alpha &\to \int d\mathbf{r} \left[\frac{\partial \varepsilon_G(\rho)}{\partial \rho} \right] , \end{aligned} \tag{15}$$

TABLE I. Factors defined in Eqs. (8) and (9) which multiply the uniform kinetic and exchange energies per particle. The present calculations are based on Eqs. (10) and (11).

	He		Ne		Ar		H_2	
Source	S_k	S_{ex}	S_k	S_{ex}	S_k	S_{ex}	S_k	S_{ex}
Gordon and Kim[a]	1	1	1	1	1	1	1	1
Waldman and Gordon[b]	1.1125	0.772	1.075	0.816	1.060	0.962	1.1125	0.772
Le Sar[c]	1.1125	0.772	1.075	0.962	1.060	0.962	1.1125	0.772
Lloyd and Pugh[d]	1	0.132	1	0.403	1	0.403	1	0.132
Present work	1.1175	0.422	1.092	0.697	1.075	0.688	1.168	0.422

[a] Reference 2.
[b] Reference 8.
[c] Reference 9.
[d] Reference 7.

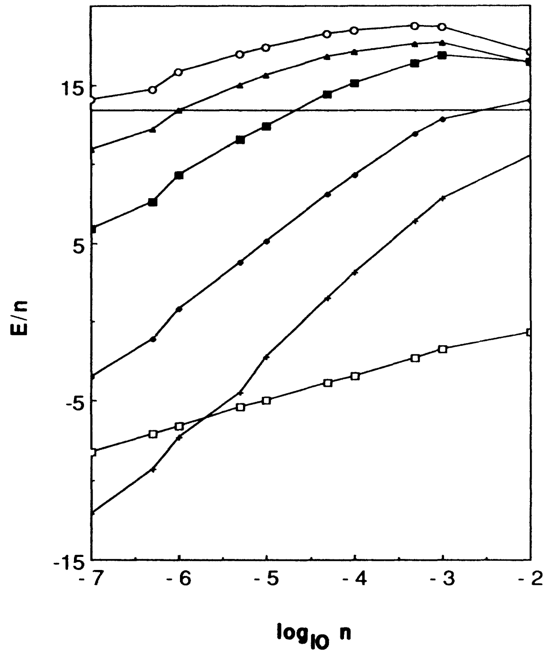

FIG. 1. The ratio $\alpha(n)$ defined by Eq. (14) in terms of the immersion energy E of a He atom into jellium of density n. Atomic units are used. The calculations shown are made with the energy functional chosen here (filled squares), Waldman and Gordon (filled diamonds), Lloyd and Pugh (filled triangles), and Gordon and Kim (pluses). The contribution to α of correlation alone is shown as empty squares and that due to kinetic and exchange energy together as circles. The horizontal line is the value computed in Ref. 22 (or 23), valid in the small-n limit.

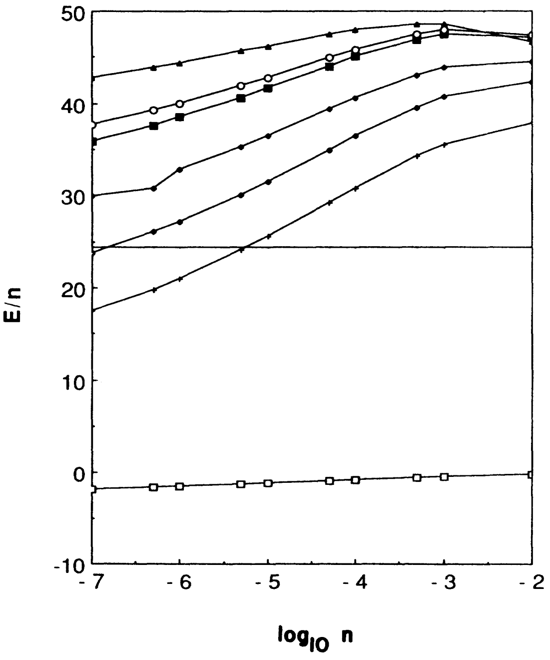

FIG. 2. Same as Fig. 1 except for Ne and an additional symbol: Le Sar (open diamonds).

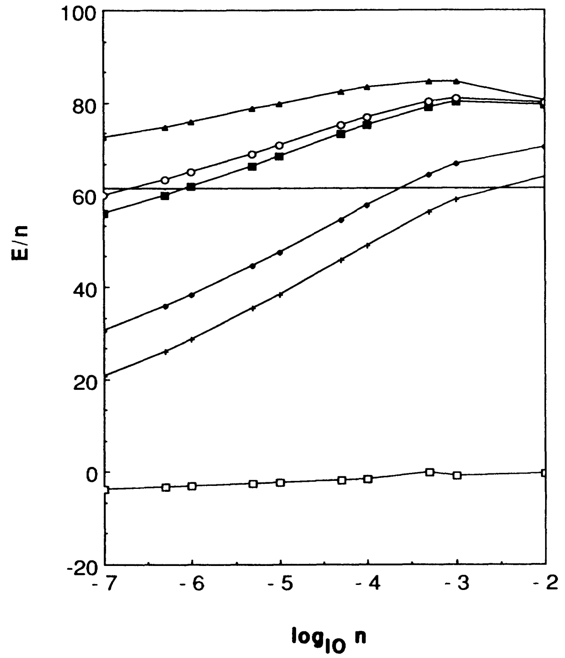

FIG. 3. Same as Fig. 1 except for Ar.

where the derivatives are evaluated at the unperturbed local atomic density. α_{kx} values from Eq. (15) for He, Ne, Ar, and H_2 are 13.8, 34.9, 58.0, and 18.2 a.u., respectively. These values agree well with those calculated at $n=10^{-7}$ a.u. as we see in Fig. 1–4 (open circles).

Note in Figs. 1 and 4 that the original GK method fails completely (except for Ne), giving an incorrect sign for

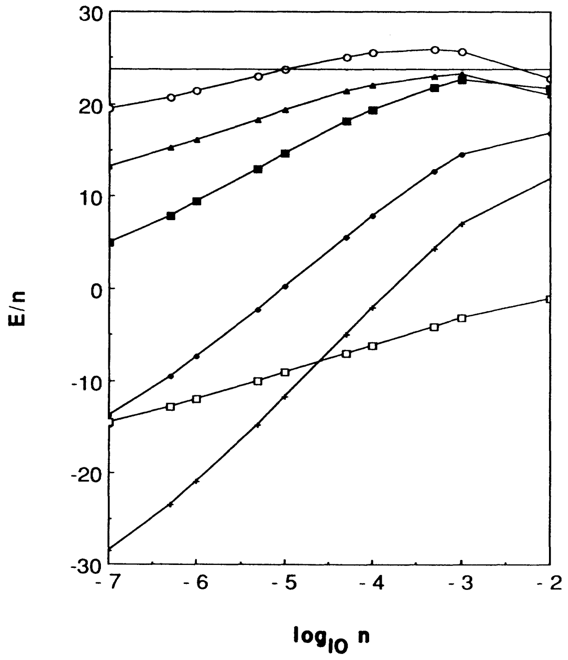

FIG. 4. Same as Fig. 1 except for H_2.

He and H_2. The Waldman-Gordon approach tends to yield a value which is too small. The present model and that of Lloyd and Pugh tend to yield reasonable results overall. The relative success of these latter models for jellium (and for interatomic interactions in the case of the Lloyd-Pugh approach) suggests their potential utility in the adsorption problem. In a subsequent paper, we plan to report positive results in this direction.[26]

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