Effect of nonadditive forces on the binding of closed-shell adsorbates on closed-shell substrates. I. Ar/Ar(100)

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A local-density approach, introduced by Gordon and Kim, is used to assess the effects of nonpair forces on the binding of closed-shell atoms on closed-shell surfaces. The nonpair effects enter the kinetics, exchange, and correlation contributions to the potential. Calculations are performed for an Ar atom bound at various sites on a (100) Ar surface. These effects modify the binding energies by as much as $\sim 12\%$ and the barrier to surface mobility by $\sim 70\%$. The magnitude of these deviations indicates a real need for further first-principles calculations.

I. INTRODUCTION

The calculation of the properties of closed-shell atoms adsorbed on closed-shell-atom surfaces has a long history. All previous work has been based on the summation of a two-body potential acting between the adsorbate and each of the atoms of the surface. The potential is generally taken to be of the Lennard-Jones or Morse form, and its parameters determined from gas-phase data and standard combination rules.

Various early workers[1] calculated the heats of adsorption of rare-gas atoms on alkali halide surfaces and obtained qualitative agreement with experiment. More recently, computers have allowed the inclusion of large numbers of substrate atoms and revived interest[2] in such calculations. In particular, the adsorption of rare-gas atoms on rare-gas surfaces has been a frequent subject of investigation.[3,4] Adsorption on imperfect surfaces has also been considered.[5] Recent experimental work[6] on He-layer adsorption has further stimulated such calculations.[7]

The aim of this paper is to investigate, in a simple way, the fundamental premise of all the previous calculations, i.e., the legitimacy of summing two-body potentials to obtain the adsorbate potential-energy surface. An approach recently developed by Gordon and Kim[8] for diatomic molecules of closed-shell species is used to treat the dominant interaction mechanisms in a way which allows the adsorbate atom to interact with the surface as a whole. The results obtained can then be compared with those of the two-body interaction approach.

The local-density approximation used by Gordon and Kim, and in this paper, lacks a firm theoretical basis. For example, the magnitude of density-gradient terms has not yet been investigated.[9] The accuracy of the approximation can thus only be surmised from qualitative general arguments,[8,9] its success in treating closed-shell diatomics,[8] and its success in work-function[10] and chemisorption calculations.[11] The results presented below indi-

cate that in the local-density approximation, at least, nonpair effects are important for the argon physical adsorption situation. Our use of the local-density approximation in this context is speculative and *a posteriori* justification is required. Further first-principle calculations are, therefore, indicated.

It is, at least, plausible that nonadditive potentials are significant in this surface problem. Calculations which involve the summation of pair potentials predict the crystal structures of the rare-gas solids to be all hexagonally close packed. With the exception of He, they are all, in fact, face-centered cubic. Various perturbation calculations on model systems have attempted to explain this discrepancy. Early efforts[12] involved third-order perturbation calculation of the induced-dipole interactions between three nonoverlapping atoms, i.e., an extension of the $1/R^6$ van der Waals interaction obtained in a second-order theory. These third-order effects were found to contribute $\sim 5\%$ of the cohesive energy of rare-gas solids and to differ by less than 0.1% in the fcc and hcp structures. Analogous perturbation calculations[13] which include short-range exchange effects show that these effects are an order of magnitude larger and more structure dependent. Short-range effects have also been investigated for the three- and four-helium-atom systems using a self-consistent-field–linear combination-of-atomic-orbitals–molecular-orbital (SCF-LCAO-MO) procedure.[14] Heavy-rare-gas-atom configurations have been studied in only a very approximate way.[15] The previous calculations thus indicate that short-range effects are probably of most importance and we shall therefore ignore nonpair effects in the long-range dispersion potentials.

Unfortunately, the experimentally measured binding curves for even the interaction of various isolated pairs of closed-shell atoms are very difficult to calculate.[16] At large distances, perturbation theory yields the correct dispersion potential, but it fails at short and intermediate distances. At

short distances, self-consistent-field calculations are accurate and yield the correct repulsion.[17] In the intermediate range, near the binding minimum, only elaborate configuration-interaction calculations may be successful. The only example of such a calculation, however, is the recent one[18] for the He-He interaction.

Gordon and Kim[8] have recently introduced a new approach to this pair-interaction problem. They used a local-density approximation[9] in which the kinetic, exchange, and correlation contributions to the total energy of the two interaction atoms are obtained by integrating a local energy function which depends only on the total electron density at any point in space. The functional forms of these contributions to the local energy are obtained from the theory of the homogeneous electron gas.[19] The relevant electron densities are taken from Hartree-Fock calculations on the isolated atoms.[20] These electron densities are also used to calculate the direct Coulomb contribution to the energy. The calculated positions and depths of the potential minima are in good agreement with scattering results for a variety of pairs of interacting atoms and ions. The long-range van der Waals tail to the potential is, of course, not obtained, since unperturbed wave functions are the only input to the calculation.

Here a similar local-density approximation is used to consider the adsorbate-surface interaction. Each of the substrate atoms and the adsorbate atom contribute to the total electron density which enters the local-density functional. Since that functional is not linear in the density, the results include effects not included in the pair-interaction approximation.

An interpolation formula is used to join a long-range van der Waals potential to the interaction between the adsorbate and the substrate atom. Thus, non-pair-wise effects are investigated only in the short- and intermediate-range contributions. The van der Waals potential is added in order to assess the importance of these effects on the total potential energy of the adsorbate.

A calculation is presented for the adsorption potential of an Ar atom above a (100) Ar surface. Binding curves for positions (a) directly above a surface atom, (b) directly above an atom in the penultimate layer, and (c) directly above the position which determines the adsorbate's lateral mobility, are obtained. These are compared with analogous results obtained using the pair-interaction model.

In Sec. II, the local-density approach to diatomic bonding is summarized. In Sec. III it is then modified to allow the treatment of adsorption, and the results for the binding of atomic Ar on an Ar surface are presented.

II. GORDON-KIM FORMALISM

Gordon and Kim[8] based their treatment of the forces between closed-shell atoms on the assumption that no rearrangement of the separate atomic densities occurs when the atoms are brought together. They calculate the direct Coulomb interaction V_C between the atoms using point nuclear charges and Hartree-Fock wave functions. Kinetic (V_{KE}), exchange (V_{EX}), and correlation (V_{COR}) contributions to the total potential (V_{TOT}) are calculated using these same wave functions in local-density functionals [$E_{KE}(\rho)$, $E_{EX}(\rho)$, and $E_{COR}(\rho)$, respectively]. These functionals are then integrated over all space.

In calculating each of these contributions, it is essential to subtract the energy of the separated atoms directly in each relevant integrand. This eliminates the need to obtain the extremely high accuracy which would be required if differences between relatively large numbers were used to obtain the binding potential.

The Hartree-Fock wave functions are taken from Clementi's tables[20] from which they can be expressed as a sum, i.e.,

$$\psi_{nl}(r - R_\alpha) = \sum_i a_n^i e^{(-\zeta_n |r - R_\alpha|)} r^{n-1} , \tag{2.1}$$

where n is the principal quantum number, l designates the orbital character of the electron, and R_α is the position of the nucleus. The electron density associated with the atom is then given

$$\rho_\alpha(r) = \left| \sum_{n\lambda} \psi_{n\lambda}(r - R_\alpha) \right|^2 , \tag{2.2}$$

where the sum runs over occupied orbitals.

The total direct Coulomb energy of two atoms a and b is given in Hartree units by

$$E_C = \frac{Z_a Z_b}{R} + \frac{1}{2} \iint \frac{[\rho_a(r_1) + \rho_b(r_1)][\rho_a(r_2) + \rho_b(r_2)]}{r_{12}} dr_1 dr_2 - Z_a \int \frac{[\rho_a(r_1) + \rho_b(r_1)]}{r_{1a}} dr_1 - Z_b \int \frac{[\rho_a(r_1) + \rho_b(r_1)]}{r_{1b}} dr_1 , \tag{2.3}$$

where the first term on the right-hand side gives repulsion between nuclei, the second term represents electron-electron repulsion, and the third and fourth terms include attractions between electrons and nuclei. Here Z_a and Z_b are the nuclear charges of atoms a and b, R is the distance between the nuclei, r_{12} is the distance between two electrons, and r_{1a} and r_{1b} are electron-nuclear distances. Similarly, the Coulomb energies of the separate atoms are

$$E_C(a) = \tfrac{1}{2} \int [\,\rho_a(r_1)\rho_a(r_2)/r_{12}] dr_1 \, dr_2$$
$$-Z_a \int [\,\rho_a(r_1)/r_{1a}] dr_1 \,, \qquad (2.4)$$

$$E_C(b) = \tfrac{1}{2} \int [\,\rho_b(r_1)\rho_b(r_2)/r_{12}]\, dr_1 \, dr_2$$
$$-Z_b \int [\,\rho_b(r_1)/r_{1b}]\, dr_1 \,. \qquad (2.5)$$

By subtracting the atomic energies from the total
energy, Gordon and Kim get the Coulomb interac-
tion

$$V_C = \frac{Z_a Z_b}{R} + \iint \frac{\rho_a(r_1)\rho_b(r_2)}{r_{12}}\, dr_1 \, dr_2$$

$$-Z_b \int \frac{\rho_a(r_1)}{r_{1b}}\, dr_1 - Z_a \int \frac{\rho_b(r_2)}{r_{2a}}\, dr_2 \,. \qquad (2.6)$$

Gordon and Kim then combine these four terms
into a single integrand, and change to a spherical
polar-coordinate system for each position vector.
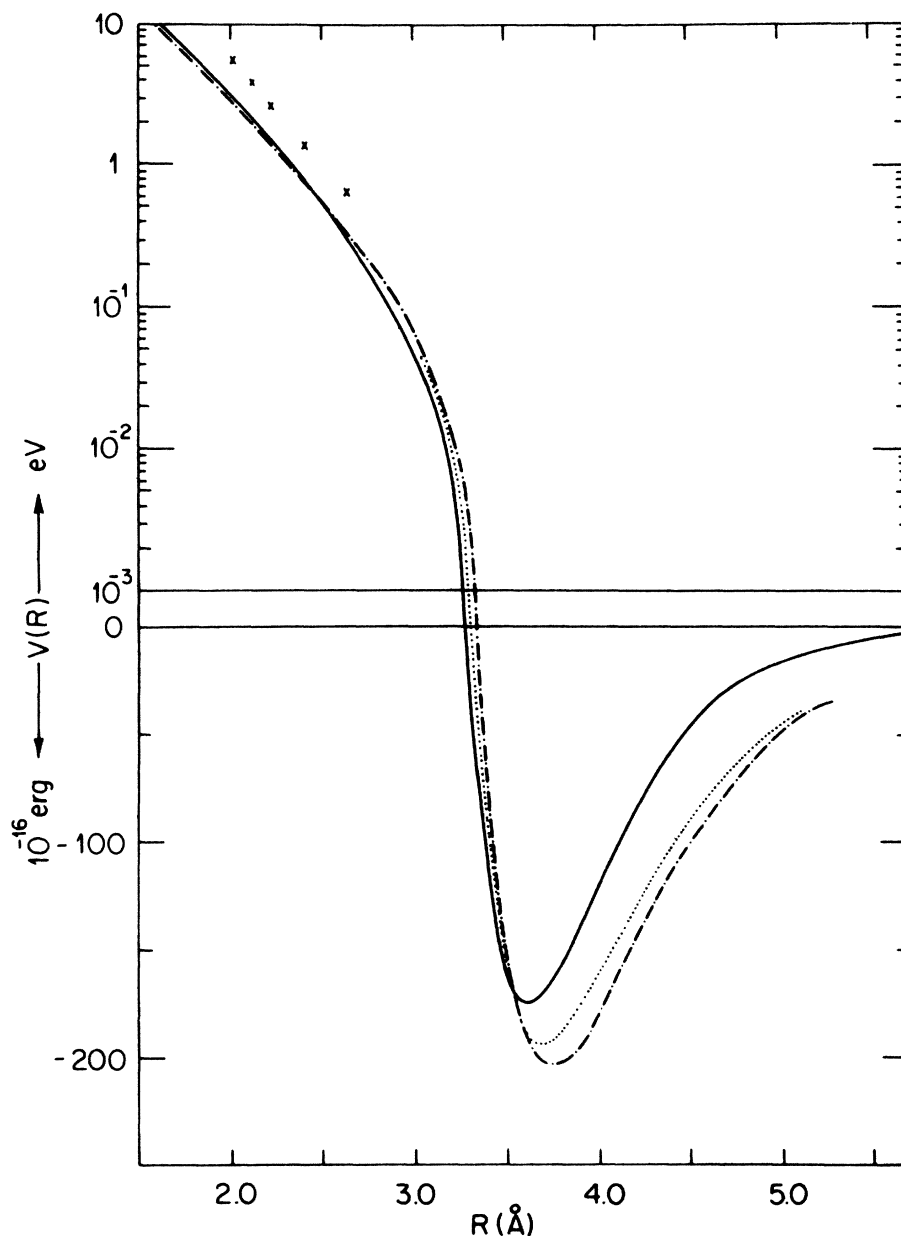After some manipulation, they express the Coulomb
interaction as

FIG. 1. From Ref. 8. Ar–Ar pair potential: (—) calculated by Gordon and Kim; (—·—) J. Barker and A. Pompe [Aus-
tralian J. Chem. 21, 1683 (1968)] (gas experiments); (···) J. M. Parson and Y. T. Lee [Third International Symposium
On Molecular Beams, June 29, 1971, Cannes (unpublished)] (beam scattering);(××) Ref. 17 (molecular Hartree Fock).

$$V_C = \int_0^\infty 4\pi r_1^2 \, dr_1 \int_0^\infty 4\pi r_2^2 \, dr_2 \, \rho_a(r_1)\rho_b(r_2) I \, , \quad (2.7)$$

where

$$I = 1/R + F(R, \, r_1 r_2) - 4/(R + r_1 + |R - r_1|) \quad (2.8)$$

for the homonuclear case, and

$$I = 1/R + F(R, \, r_1, \, r_2) - 2/(R + r_1 + |R - r_1|)$$

$$- 2/(R + r_2 + |R - r_2|) \quad (2.9)$$

for the heteronuclear case. Here

$$F(R, \, r_1, \, r_2) = 2/(R + r_1 + |R - r_1|) \, , \quad r_2 < |R - r_1|$$

$$F(R, \, r_1, \, r_2) = \tfrac{1}{2}(1/r_1 + 1/r_2) - R/4r_1 r_2$$

$$- (r_1 - r_2)^2/4Rr_1 r_2 \, ,$$

$$|R - r_1| < r_2 < R + r_1$$

$$F(R, \, r_1, \, r_2) = 1/r_2 \, , \quad r_2 > R + r_1 \, . \quad (2.10)$$

The kinetic, exchange, and correlation local-energy-density functionals E_i are obtained from standard homogeneous-electron-gas theory in Hartree units as

$$E_{KE}(\rho) = \tfrac{3}{10}(3\pi^2)^{2/3}\bar\rho^{\,2/3}, \quad (2.11)$$

$$E_{EX}(\rho) = -\tfrac{3}{4}(3/\pi)^{1/3}\bar\rho^{\,1/3} \, , \quad (2.12)$$

and

$$E_{COR}(\rho) = -0.438 r_s^{-1} + 1.325 r_s^{-3/2}$$

$$- 1.47 r_s^{-2} - 0.4 r_s^{-5/2}, \quad r_s > 10 \, ;$$
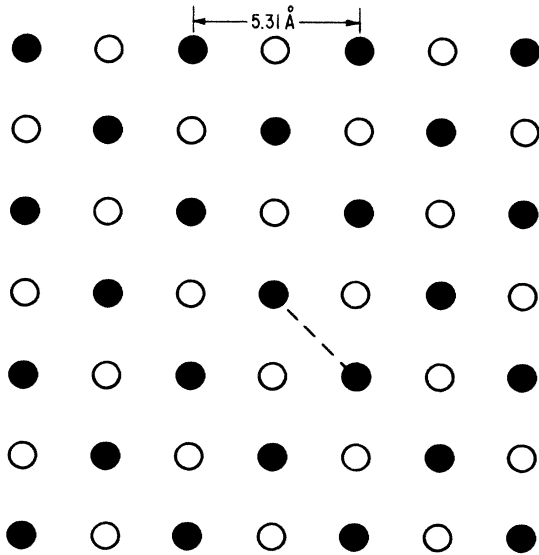
FIG. 2. The (100) face of an fcc crystal. The open circles represent the atoms in the surface layer; the solid circles (—) represent those in the penultimate layer. The layers alternate. The dashed path is the one for lateral adsorbate mobility.

$$E_{cor}(\rho) = 0.06156 - 0.01898 \ln r_s, \quad 10 > r_s > 0.7$$

$$E_{cor}(\rho) = 0.0311 \ln r_s - 0.048$$

$$+ 0.009 r_s \ln r_s - 0.01 r_s \, , \quad 0.7 > r_s \, . \quad (2.13)$$

Here,

$$r_s = (3/4\pi\bar\rho)^{1/3} \, , \quad \bar\rho = \rho a_B^3 \, ,$$

and a_B is the Bohr radius. The intermediate-regime expression is an interpolation formula. Each of these functionals contributes a term V_i to the interaction energy,

$$V_i = \int d\vec r \, \{[\, \rho_a(r) + \rho_b(r)]E_i(\rho_a + \rho_b)$$

$$- \rho_a(r)E_i(\rho_a) - \rho_b(r)E_i(\rho_b)\} \, . \quad (2.14)$$

These integrals are evaluated numerically using a spheroidal coordinate system in which the ϕ integration is trivial since the integrand has azimuthal symmetry.

Reasonable agreement with experiment was obtained for a variety of pairs of interacting closed-shell species, e.g., Ne^2, Ar^2, Kr^2, Ne-Ar, Kr-Ar, and K^+-Cl^-, etc. The results for the Ar-Ar potential are shown together with some scattering results in Fig. 1 which is taken from Ref. 8.

III. APPLICATION TO ADSORBATE-SUBSTRATE INTERACTION

Each atom of the (100) argon fcc substrate is represented by its Hartree-Fock wave function. A representation of the surface is shown in Fig. 2 where solid circles represent atoms in the ultimate layer and open circles—those in the penultimate layer. The charge density ρ_a of Sec. II is taken to represent the adsorbate density. ρ_b is now, however, given by

$$\rho_a = \sum_i \rho_i \quad (3.1)$$

where the summation extends over all the substrate atoms.

The direct Coulomb interaction between the densities due to adsorbate and the surface atoms [Eq. (2.7)] is linear in each of those densities. Thus a pair-wise summation of the interactions between the adsorbate and each surface atom is adequate.

The kinetic, exchange, and correlation contributions [Eqs. (2.11)–(2.14) are nonlinear in the densities and thus, they must be treated in a non-pair-wise manner. The integrals of Eq. (2.14) are now essentially three dimensional due to the absence of complete azimuthal symmetry. Considerable computational care is required to ensure that the quan-
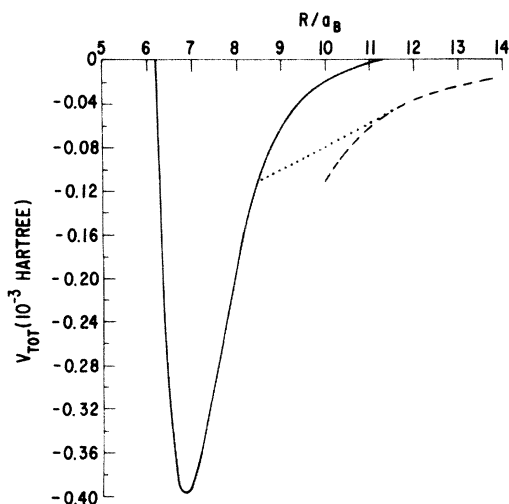
FIG. 3. (—) Ar-Ar pair potential as calculated by Gordon and Kim (Ref. 8); (---) van der Waals tail of standard Lennard-Jones fit to Ar-Ar pair potential; (···) interpolation between the Gordon-Kim and van der Waals regimes.

tities calculated are sufficiently accurate to be meaningfully compared with the results of a conventional pair-wise calculation.

The calculated total interaction between two Ar atoms is shown by the solid curve in Fig. 3. The dashed line is the long-range van der Waals interaction given in a standard Lennard-Jones repre-

sentation of the potential[21]

$$V_{vdW} = - 109.4909/R^6 \text{ hartree,} \tag{3.2}$$

where R is in units of the Bohr radius. The dotted line is a linear extrapolation used to connect the calculated and van der Waals contributions to the total potential. The results presented below were found to be quite insensitive to the detailed nature of the extrapolation used. The total pair potential is then taken as calculated by Gordon and Kim for separations less than 8.5 Bohr radii, as the dotted line for separations between 8.5 and 12 Bohr radii, and as the dashed line for separations greater than 12 Bohr radii.

For each of three lateral positions on the surface lattice, two binding curves were calculated. Each gives the interaction potential as a function of the adsorbate distance from the surface plane. The first curve is based on the use of the total pair-interaction potential of Fig. 3 to sum the interaction between the adsorbate atom and each of over 500 atoms of the substrate.

The second curve was obtained by summing the extrapolated van der Waals and Coulomb contributions over the same set of substrate atoms. The full results for the kinetic, exchange, and correlation contributions were obtained by including all substrate atoms within 12 Å of the adsorbate in the density sum of Eq. (3.1). These were then added to the Coulomb and van der Waals contributions.
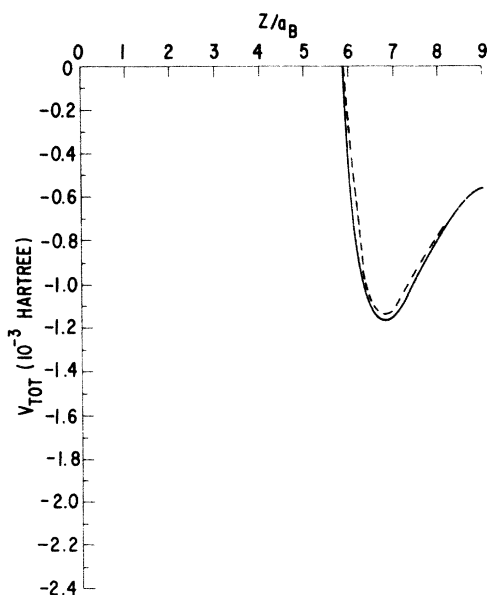

FIG. 4. Binding potential of an Ar atom over a surface atom on a (100) Ar surface. (—) as calculated by summing pair-interaction potentials. (---) as calculated in the nonadditive treatment.
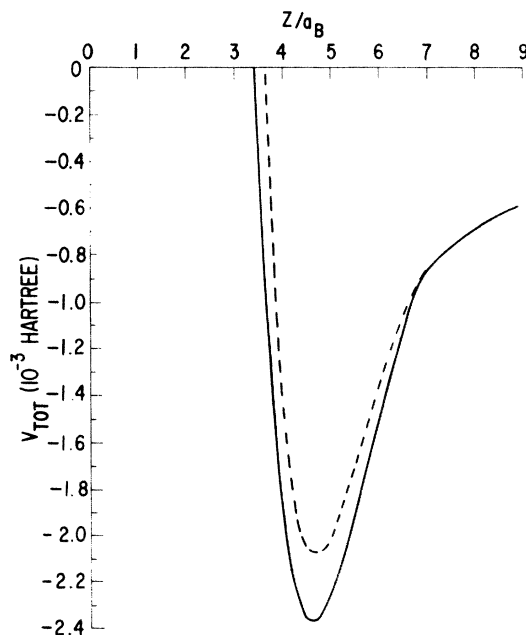

FIG. 5. Binding potential of an Ar atom over an atom in the penultimate layer of a (100) Ar surface. (—) as calculated by summing pair-interaction potentials. (---) as calculated in the nonadditive treatment.
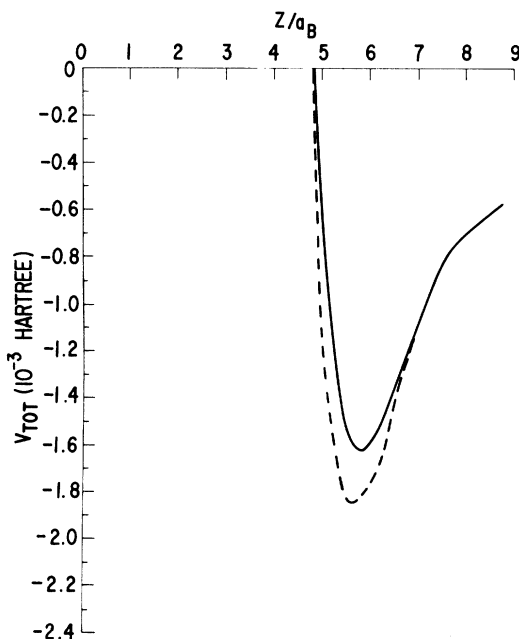
FIG. 6. Binding potential of an Ar atom over the midpoint between two atoms in the surface layer of a (100) Ar surface. (—) as calculated by summing pair-interaction potentials. (---) as calculated in the nonadditive treatment.

The full curves were calculated with an accuracy of about 10^{-5} hartree. Higher precision could be obtained with a concomitant increase in computer costs.

Figure 4 shows the curves for adsorption directly over a surface atom. The two curves are essentially identical. No significant effects of the non-additive potential appear. The atom directly under the adsorbate dominates the interaction.

Figure 5 shows the two curves for a site directly over an atom in the penultimate layer. This is, of course, the site of maximum binding. The full calculation shows a less tightly bound adsorbate than does the pair-wise calculations. The decrease in binding energy is $(0.30 \pm 0.02) \times 10^{-3}$ hartree, i.e., about 12% of the pair result.

Figure 6 shows the two curves for binding directly over the midpoint between two nearest-neighbor surface atoms. The binding over this position is crucial in determining the lateral adsorbate mobility. It is most likely that atoms pass from one site of maximum binding to another over the path shown

in Fig. 2. The results of the full calculation for this site show a stronger binding than those of the pair-wise calculation. The increase in binding energy is $(0.21 \pm 0.04) \times 10^{-3}$ hartree.

Thus, the barrier calculated using the curves obtained from a pair-wise calculation is found to be 0.73 hartree. The full calculation yields a barrier of $(0.23 \pm 0.04) \times 10^{-3}$ hartree, i.e., about 31% of the pair result.

The positions of the binding maxima are changed by less than 3% in all three cases as are the force constants of parabolic fits to the potentials near the minima.

IV. DISCUSSION

The present calculation has been restricted to a single adsorbate species on a given crystal surface. Nonadditive effects in the kinetic, exchange, and correlation contributions to the total potential have been included. No such effects in the dispersion forces have been considered.

The results have been obtained within the local-density approximation. That approximation has been shown to be adequate by Gordon and Kim in treating diatomics of closed-shell species. There is, however, a need to consider the effect of higher-order density-gradient terms in the energy-density functional on many-atom calculations. Within this approximation it has been demonstrated that nonadditive forces can have a significant effect on the properties of rare-gas atom adsorbed on rare-gas surfaces. In the case of Ar adsorbed on (100) Ar, the effects on both the binding energies and lateral mobility of the adsorbate are quite large. Systematic experimental and theoretical studies on a wide range of systems are now required. There is a real need for first-principles calculations to further investigate these effects. Both atomic-beam diffraction studies and consideration of the second virial coefficient of adsorbed layers may prove quite useful.[22]

In a future paper, the Gordon-Kim approach will be applied to the prediction of rare-gas crystal structures. There, the relevant experimental data is readily available.

[1]See, e.g., J. E. Lennard -Jones and B. M. Dent, Trans. Faraday Soc. 24, 92 (1928); Trans. Faraday Soc. 28, 333 (1932); W. J. C. Orr, Trans. Faraday Soc. 35, 1247 (1939); F. C. Tompkins and D. M. Young, Trans.

Faraday Soc. 47, 77 (1951); D. M. Young, Trans. Faraday Soc. 47, 1228 (1951).
[2]See, e.g., T. Ron and M. Folman, J. Phys. Chem. 75, 2602 (1971); J. Phys. Chem. 75, 532 (1971).

[3]W. A. Steele and M. Ross, J. Chem. Phys. 35, 850 (1961); J. Chem. Phys. 35, 862 (1961); J. Chem. Phys. (1961); J. Chem. Phys. 35, 871 (1961); W. A. Steele and E. R. Kebbekus, J. Chem. Phys. 43, 292 (1965).

[4]F. Ricca, Nuovo Cimento Suppl. 5, 339 (1967); H. E. Neustadter and R. J. Bacigalupi, Surf. Sci. 6, 246 (1967).

[5]C. Pisani and F. Ricca, J. Vac. Sci. Tech. 9, 926 (1971).

[6]See, e.g., J. G. Dash and M. Bretz, Phys. Rev. 174, 247 (1968).

[7]A. D. Novaco and F. J. Milford, J. Low Temp. Phys. 3, 307 (1970); F. Ricca, C. Pisani, and E. Garrone, J. Chem. Phys. 51, 4079 (1969).

[8]R. G. Gordon and Y. S. Kim, J. Chem. Phys. 56, 3122 (1972).

[9]See, e.g., P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965); 145, 561 (1966).

[10]See, e.g., N. D. Lang and W. Kohn, Phys. Rev. B 3, 1215 (1971).

[11]J. R. Smith, S. C. Ying, and W. Kohn, Phys. Rev. Lett. 30, 610 (1973).

[12]See, e.g., B. M. Axilrod, J. Chem. Phys. 19, 719 (1951).

[13]L. Jansen, Phys. Lett. 4, 91 (1963); Phys. Lett. 4, 95 (1963); L. Jansen, Phys. Rev. 135, A1292 (1964).

[14]O. A. Novaro and V. Beltran-Lopez, J. Chem. Phys. 56, 815 (1971).

[15]H. Margenau and J. Stamper, Advances in Quantum Chemistry (Academic, New York, 1967), Vol. 3, p. 129.

[16]J. O. Hirschfelder and W. J. Meath, Adv. Chem. Phys. 12, 3 (1967).

[17]See, e.g., T. L. Gilbert and A. C. Wahl, J. Chem. Phys. 47, 3425 (1967).

[18]P. Bertoncini and A. C. Wahl, Phys. Rev. Lett. 25, 991 (1970).

[19]D. Pines, Elementary Excitations in Solids (Benjamin, New York, 1963).

[20]E. Clementi, IBM J. Res. Dev. Suppl. 9, 2 (1965).

[21]E. R. Dobbs and G. O. Jones, in Reports on Progress in Physics, edited by A. C. Stickland (The Physical Society, London, 1957), Vol. 20, p. 516.

[22]W. A. Steele (unpublished).