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# Electron-Gas plus Damped-Dispersion Model for Intermolecular Forces. The Rare-Gas and H<sub>2</sub>-He, H<sub>2</sub>-Ne, and H<sub>2</sub>-Ar Potentials

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The modified Gordon-Kim (MGK) electron-gas model for the calculation of the short-range repulsive interactions between closed-shell atoms and molecules is used with a damped-dispersion term of a form suggested by Hepburn et al. to calculate the intermolecular potentials between the rare-gas atoms and H<sub>2</sub>-He, H<sub>2</sub>-Ne, and H<sub>2</sub>-Ar. The damping function for the dispersion energies is found by comparison with the experimental Ar-Ar potential and is then used without change for all other interactions. Except for interactions involving Ne atoms, the results for the atom-atom interactions are uniformly quite good, with an average deviation from experiment in the position of the minimum (neglecting those involving Ne atoms) of only 0.7%. Both the radial  $V_0(r)$  and anisotropic  $V_2(r)$  terms of the atom-molecule results are compared with experiment. The calculated  $V_0(r)$  potentials for He-H<sub>2</sub> and Ar-H<sub>2</sub> show close agreement with experiment, though the  $V_2$  terms are less well determined. All interactions involving Ne atoms are too repulsive. The errors in the potentials involving Ne atoms are attributed to errors in the treatment of the exchange energy in the MGK model.

## I. Introduction

Despite the fundamental importance of intermolecular interactions in the study of the properties of solids, liquids, and gases, our knowledge of the forces between atoms and molecules is rather limited. Experimental determinations are available for many atom-atom and a few atom-linear molecule interactions, but for the more complicated molecule-molecule systems, only the spherical parts of the pair potentials are well characterized. Theoretically, much has been learned about the different regimes of the potential curves;<sup>1</sup> however, the short-range repulsive parts of the potentials remain difficult to evaluate. Some results using Hartree-Fock self-consistent-field (SCF) calculations are available, but this method is severely limited by the difficulty of the SCF calculations, especially for larger systems. A variety of semi-empirical schemes have been proposed, but cannot be used with confidence in a predictive way. Probably the most useful approach has been the use of the Gordon-Kim (GK) electron-gas model.<sup>2</sup> In the original formalism, and a later modified version (MGK),<sup>3</sup> this model has been shown to give pair potentials (and structures and energies of ionic crystals<sup>4</sup>) in generally good agreement with experimental data. Since the energy is expressed as a simple functional of the electronic density, which is taken as a superposition of densities calculated from SCF calculations on the isolated molecules, it takes much less computer time per potential point than other ab initio methods. Despite its many successes, however, serious problems with the model remain, especially when applied to neutral systems where the binding is due to the dispersion (van der Waals) interactions.

In its usual formulation, the electron-gas model includes a term corresponding to the correlational interaction energy. A weakness of the model is that this term has an exponential form at long range instead of the asymptotic  $-C_6/r^6$  form of the dispersion energy. A number of ways of correcting for this problem have been suggested; however, none have been completely successful. Rae<sup>5</sup> found that adding the dispersion term directly to the GK energy (with correlation) gave potential energy wells that were over bound. Cohen and Pack<sup>6</sup> presented a way to match the long-range forms

to the correlational energy in the vicinity of the potential minimum. However, it is unclear exactly where the long-range forms are no longer valid. Gordon and co-workers<sup>7,8</sup> combined the GK model with the Drude model<sup>9</sup> to give a unified theory; however, the dispersion interactions were only included up to the  $C_6/r^6$  term and the agreement with experiment was not uniformly good. Finally, calculations on solid nitrogen and carbon dioxide at high pressures,<sup>10</sup> where the correlational energy was dropped completely and just the anisotropic  $C_6/r^6$  term was included, gave results in very close agreement with experiment for the pressure-volume curves, but failed to predict the proper crystal structures. We have found it necessary to include higher order dispersion terms ( $C_8$  and  $C_{10}$ ), which are more anisotropic in the N<sub>2</sub>-N<sub>2</sub> interaction than the  $C_6$  term, to get reasonable predictions of crystal structures.<sup>11</sup> However, inclusion of the higher order terms leads to potential energy wells that are too deep. The purpose of the present paper is to provide a simple way to modify the dispersion energies to include the higher order terms and still get accurate predictions of the interaction potential.

It is well-known that the long-range forms of the dispersion energy are no longer valid in the region of the potential well. A number of models have been proposed to deal with this problem, including the electron-gas-Drude model mentioned above. Tang and Toennies<sup>12</sup> introduced a method to correct for the decrease in the dispersion energies at short distances based on a Drude model analysis, but including terms up to  $r^{-10}$ . We choose, however, to follow the work of Hepburn, Scoles, and Penco (HSP),<sup>13</sup> who introduced an entirely empirical damping function to multiply the dispersion energy to give it the proper behavior when used in conjunction with SCF short-range potentials. Scoles and co-workers have presented improvements to the original scheme,<sup>14,15</sup> but for the present we shall take the approach used in the earlier work.<sup>13</sup> We note that empirical functions such as used by Scoles and co-workers and in the present work have no

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(9) J. O. Kirschfelder, C. F. Curtis, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, 1954.

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(12) K. T. Tang and J. P. Toennies, *J. Chem. Phys.*, **66**, 1496 (1977); **68**, 5501 (1978); **74**, 1148 (1981).

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(14) C. Douketis, G. Scoles, S. Marchetti, M. Zen, and A. J. Thakkar, *J. Chem. Phys.*, **76**, 3057 (1982).

(15) W. R. Rodwell and G. Scoles, *J. Phys. Chem.*, **86**, 1053 (1982).

TABLE I: Correction Factors<sup>a</sup>

	correction factor		correction factor		
	kinetic	exchange	kinetic	exchange	
HeHe	1.1125	0.772	NeXe	1.056	0.903
HeNe	1.094	0.794	ArAr	1.060	0.962
HeAr	1.086	0.862	ArKr	1.052	0.981
HeKr	1.078	0.879	ArXe	1.048	0.981
HeXe	1.074	0.879	KrKr	1.045	1.0
NeNe	1.075	0.816	KrXe	1.041	1.0
NeAr	1.067	0.886	XeXe	1.037	1.0
NeKr	1.060	0.903			

<sup>a</sup>The correction factors for like interactions (He–He, etc.) are from ref 3. The factors for unlike interactions differ from those in ref 3 and were determined by  $F_{AB} = (F_{AA}F_{BB})^{1/2}$ , as discussed in text.

physical significance and are chosen for ease of calculation. Below we shall find a form for the damping function by comparing the MGK potential with the experimental Ar–Ar potential. We shall then use this damping function and generate all the rare-gas interactions and the H<sub>2</sub>–He, H<sub>2</sub>–Ne, and H<sub>2</sub>–Ar potentials. As we shall see, the agreement with the experiment is generally quite good. Unless noted, all quantities will be given in atomic units.<sup>16</sup>

## II. Methods

*A. Electron-Gas Model.* The basic assumptions of the GK model<sup>2</sup> are that the total electronic density of a system can be approximated by a superposition of the densities of the constituent atoms or molecules (additive density approximation) and that the energy functionals for a uniform electron gas give a good description of the energy. The short-range interaction energy between two closed-shell atoms or molecules is given by

$$W_{\text{GK}} = \int \{E[\rho_a + \rho_b] - E[\rho_a] - E[\rho_b]\} d\vec{r} \quad (1)$$

where

$$E[\rho(\vec{r})] = C_k \rho^{5/3}(\vec{r}) - C_x \rho^{4/3}(\vec{r}) + E_c[\rho(\vec{r})] \quad (2)$$

Here  $\rho_a$  and  $\rho_b$  are the electronic densities of the constituent molecules and  $C_k$  and  $C_x$  are constants. The first two terms in eq 2 are the kinetic and exchange energies, respectively. The correlational energy functional,  $E_c$ , has been discussed elsewhere,<sup>2</sup> but is not included in the present study. As usually applied, the electronic densities of the constituent molecules are taken from SCF calculations on the isolated molecules.

Two sources of error in the GK model are the additive density approximation and the use of the overly simple energy–density functionals in eq 2. It has been suggested that the additive density approximation, where the total density is taken as a sum of the constituent densities, may be seriously in error.<sup>17</sup> However, because of the generally good agreement obtained by using this approximation and the difficulties introduced in trying to correct for possible errors, we shall assume that the additive density approximation holds. To correct for the errors in the functionals, we use a modification of the GK model (MGK) that scales each energy term by a constant factor that depends on the number of electrons in the interacting system. The correction factors were found by comparing the results of SCF calculations with density-functional calculations on atoms.<sup>3</sup> While correcting the inherent errors in the kinetic and correlational energies is relatively straightforward, and related to correcting for the nonuniformity of the electronic distributions, the exchange-energy functional includes an error due to overcounting the self-exchange energy. Rae<sup>6,18</sup> and Lloyd and Pugh<sup>19</sup> used a simple expression for the exchange correction factor that is derived from the form of the functional in eq 2. We choose, however, to use the MGK model

TABLE II: Dispersion Energy Coefficients<sup>a</sup>

	C <sub>6</sub>	C <sub>8</sub>	C <sub>10</sub>
HeHe <sup>b</sup>	1.461	14.11	183.6
HeNe <sup>c</sup>	3.13	32.6	429.0
HeAr <sup>c</sup>	9.82	153.5	3247
HeKr <sup>c</sup>	13.6	212.1	4334
HeXe <sup>c</sup>	18.3	357.2	8398
NeNe <sup>d</sup>	6.882	73.87	965
NeAr <sup>c</sup>	20.7	345	7730
NeKr <sup>c</sup>	28.7	504	10905
NeXe <sup>c</sup>	37.8	744	16830
ArAr <sup>g</sup>	63.60	1765	54900
ArKr <sup>c</sup>	95.5	2400	79500
ArXe <sup>c</sup>	139.22	4159	160461
KrKr <sup>d</sup>	135.11	2581	65500
KrXe <sup>c</sup>	207.24	6110	217380
XeXe <sup>d</sup>	281.15	7033.5	240247
H <sub>2</sub> He <sup>e</sup>	4.016	55.64	1001.1
H <sub>2</sub> He <sup>f</sup>	0.392	18.42	330.0
H <sub>2</sub> Ne <sup>e</sup>	8.47	128	2415
H <sub>2</sub> Ne <sup>f</sup>	0.796	38.4	724
H <sub>2</sub> Ar <sup>e</sup>	28.44	576	14610
H <sub>2</sub> Ar <sup>f</sup>	2.89	144	3651

<sup>a</sup>In atomic units. <sup>b</sup>A. J. Thakkar, unpublished calculations as reported in ref 14. <sup>c</sup>K. T. Tang, J. M. Norbeck, and P. R. Certain, *J. Chem. Phys.*, **64**, 3063 (1976). For the C<sub>8</sub> and C<sub>10</sub> coefficients, the midpoint between the reported upper and lower bounds was used. <sup>d</sup>M. B. Doran, *J. Phys. B.*, **7**, 558 (1974). <sup>e</sup>Values for C<sub>n</sub><sup>0</sup> (eq 8) from ref 15. <sup>f</sup>Values for C<sub>n</sub><sup>2</sup> (eq 8) from ref 15. <sup>g</sup>Reference 22.

since it also corrects in part for other inadequacies in the functional. However, below we do consider a modification of the Waldman–Gordon exchange term.<sup>3</sup> We also apply the correction factors in a slightly different way than earlier applications, taking the factors for the interaction of unlike species ( $F^{AB}$ ) as the geometric average of the correction factors for the interactions of the like pairs ( $F^{AA}$  and  $F^{BB}$ ), i.e.

$$F^{AB} = (F^{AA}F^{BB})^{1/2} \quad (3)$$

These correction factors are given in Table I. We use this choice of correction factors as it weights the electron density of the unlike atoms more evenly and leads to a great improvement in the prediction potentials between unlike atoms, especially those involving He atoms. The atomic electronic densities were calculated from the wave functions of Clementi and Roetti<sup>20</sup> and the H<sub>2</sub> density from the wave function reported by Cade and Wahl.<sup>21</sup>

*B. Dispersion Energies.* The total interaction potential between closed-shell atoms is written as

$$V(r) = V_{\text{GK}}(r) + f(x) V_d(r) \quad (4)$$

$$x = r/r_m$$

where  $V_{\text{GK}}$  is the sum of the MGK energy,  $W_{\text{GK}}$  in eq 1, and the Coulomb energy. The dispersion energy is

$$V_d = - \left\{ \frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} \right\} \quad (5)$$

where we truncate at the  $r^{-10}$  term since higher order coefficients are not well-known, especially for molecular systems. The dispersion coefficients used here are given in Table II. The damping function,  $f$ , is a function of both the distance and position of the minimum  $r_m$ . The form of  $f$  was found by calculating, for Ar–Ar

$$g(x) = [V_{\text{exptl}}(r) - V_{\text{GK}}(r)] / V_d(r)$$

using the experimentally determined Ar–Ar potential,  $V_{\text{exptl}}$ ,<sup>22</sup> and the MGK potential.  $g(x)$  vs.  $x$  is plotted in Figure 1. The negative region of  $g(x)$  is due in part to the requirement used in determining

(16) Distance: 1 bohr = 0.529177 Å; energy: 1 hartree = 2 Ry = 27.21163 eV = 4.35957 × 10<sup>-11</sup> erg = 3.15787 × 10<sup>5</sup> K = 2.19474 × 10<sup>5</sup> cm<sup>-1</sup>.

(17) W. Kolos and E. Radzio, *Int. J. Quantum Chem.*, **13**, 627 (1978); E. Radzio-Andzelm, *ibid.*, **20**, 601 (1981); *Chem. Phys. Lett.*, **84**, 64 (1981).

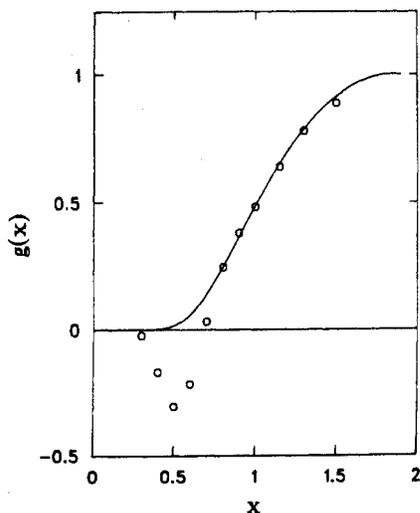
(18) A. I. M. Rae, *Mol. Phys.*, **29**, 467 (1975).

(19) J. Lloyd and D. Pugh, *Chem. Phys. Lett.*, **26**, 281 (1974).

(20) E. Clementi, and C. Roetti, *At. Data Nucl. Data Tables*, **14**, 177 (1974).

(21) P. E. Cade and A. C. Wahl, *At. Data Nucl. Data Tables*, **13**, 339 (1974).

(22) R. A. Aziz and H. H. Chen, *J. Chem. Phys.*, **67**, 5719 (1977).



**Figure 1.** The points are  $g(x)$ , the correction factor for the dispersion interaction, vs.  $x = r/r_m$ , where  $r_m$  is the position of the minimum. The derivation of  $g(x)$  is described in the text and is based on the Ar-Ar interaction. The solid line is  $f(x)$  from eq 6.

the experimental potential that the short-range part of the experimental potential be close to the SCF potential of Wahl.<sup>23</sup> It is known that SCF potentials may be too repulsive and that inclusion of correlational energies reduces the potential.<sup>24</sup> We therefore do not fit to this region, because inclusion of a negative  $f(x)$  would give a net repulsive contribution to the total energy. The solid line in Figure 1 is a fit to  $g(x)$  using the HSP<sup>13</sup> damping function

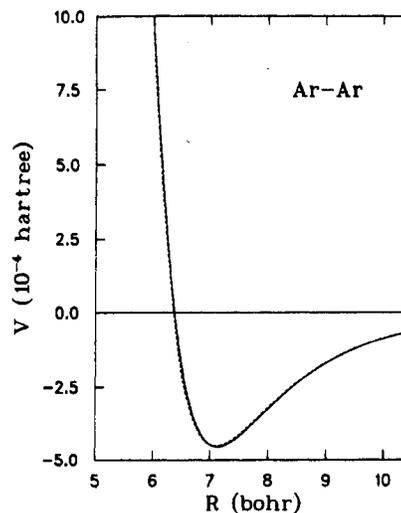
$$f(x) = \begin{cases} e^{-(\beta/x-1)^n} & x \leq \beta \\ 1 & x \geq \beta \end{cases} \quad (6)$$

The parameters found to fit the Ar-Ar data ( $\beta = 1.8$  and  $n = 1.5$ ) are quite different from the values of Hepburn et al.<sup>13</sup> ( $\beta = 1.28$  and  $n = 2$ ), because of the differences in SCF interaction potentials, upon which the HSP parameters were based, and GK potentials at large  $r$ . Because of the form of the exchange and kinetic energy terms in the GK model, potentials calculated with this model have a small spurious attractive well at large distances; thus, the damping function must extend much further beyond the potential minimum than if SCF short-range potentials were used.

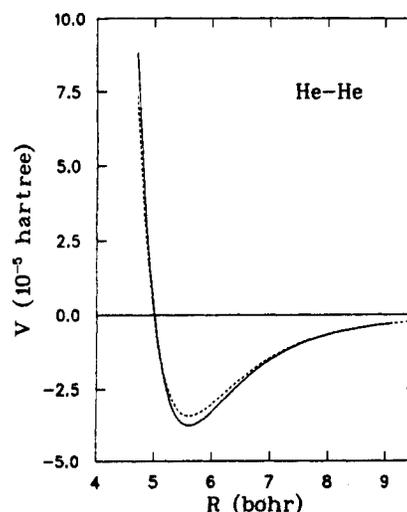
It has been mentioned previously that this form of damping function has no physical significance and indeed may be of the wrong form since a different function should perhaps multiply each term in the dispersion energy expansion.<sup>12,14</sup> However, it is a very simple expression which requires very few parameters, so is computationally fast. It may be possible to refine the results further by the use of other expressions, but considering the problems inherent in GK potentials, or indeed SCF potentials, it may not be worth the effort.

### III. Results

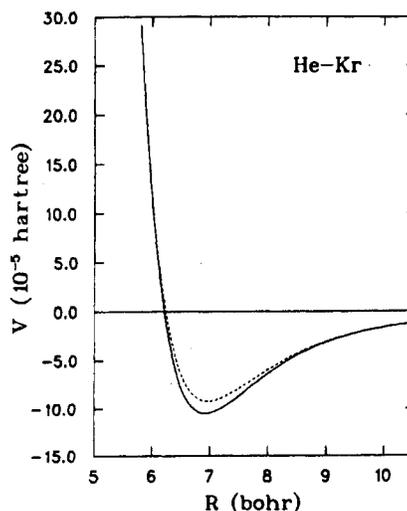
**A. Atom-Atom Potentials.** Using the GK short-range potentials calculated as described in section IIA, the dispersion coefficients given in Table I, and the damping function of eq 6, we calculated the interactions between all rare-gas pairs. The experimental potential parameters are given in Table III. The calculated values of  $\sigma$  ( $V(\sigma) = 0$ ),  $r_m$  (the position of the minimum:  $V'(r_m) = 0$ ), and  $\epsilon_m$  (the well depth:  $V(r_m) = -\epsilon_m$ ) are compared with the experimental values in Table IV. The percent deviations from the experimental results are also given. Except for interactions involving Ne atoms, the results are remarkably good. Not including the Ne interactions, the average errors in  $\sigma$ ,  $r_m$ , and  $\epsilon_m$  are 0.7%, 0.4%, and 7.2%, respectively, which are as small as or less than that found with any other theory and are within experimental errors. Some sample potentials are plotted in Figures



**Figure 2.** Well region for the Ar-Ar potential. The dashed line is the experimental result from ref 22 and the solid line is the present result.



**Figure 3.** Well region for the He-He potential. The dashed line is the experimental result (footnote b Table III) and the solid line the present result.



**Figure 4.** Well region for the He-Kr potential. The dashed line is the experimental result (footnote e Table III) and the solid line the present result.

2-7. The Ar-Ar potential in Figure 2 shows such good agreement with experiment because  $f(x)$  was derived from those data. The other calculated potentials also show quite good agreement with

(23) A. C. Wahl, unpublished calculation as reported in ref 22.

(24) P. J. Hay, R. T. Pack, and R. L. Martin, submitted to *J. Chem. Phys.*

TABLE III: Experimental Potential Parameters<sup>a</sup>

	$\sigma$	$r_m$	$10^4 \epsilon_m$
HeHe <sup>b</sup>	4.96	5.61	0.342
HeNe <sup>c</sup>	5.05	5.61	0.724
HeAr <sup>d</sup>	5.86	6.56	0.931
HeKr <sup>e</sup>	6.20	6.94	0.956
HeXe <sup>e</sup>	6.69	7.46	0.888
NeNe <sup>f</sup>	5.19	5.78	1.362
NeAr <sup>g</sup>	5.84	6.48	2.279
NeKr <sup>g</sup>	6.09	6.77	2.358
NeXe <sup>g</sup>	6.46	7.08	2.374
ArAr <sup>h</sup>	6.34	7.10	4.535
ArKr <sup>i</sup>	6.57	7.33	5.298
ArXe <sup>j</sup>	6.89	7.69	5.963
KrKr <sup>k</sup>	6.76	7.58	6.330
KrXe <sup>j</sup>	7.07	7.89	7.394
XeXe <sup>l</sup>	7.35	8.24	8.942
H <sub>2</sub> He, V <sub>0</sub> <sup>m</sup>	5.67	6.39	0.489
H <sub>2</sub> He, V <sub>2</sub> <sup>m</sup>	6.61	7.28	0.029
H <sub>2</sub> Ne, V <sub>0</sub> <sup>n</sup>	5.52	6.24	1.040
H <sub>2</sub> Ne, V <sub>2</sub> <sup>n</sup>	6.07	6.77	0.092
H <sub>2</sub> Ar, V <sub>0</sub> <sup>o</sup>	6.00	6.75	2.318
H <sub>2</sub> Ar, V <sub>2</sub> <sup>o</sup>	6.35	7.07	0.261

<sup>a</sup>In atomic units, with  $V(\sigma) = V'(r_m) = 0$  and  $V(r_m) = -\epsilon_m$ . <sup>b</sup>R. A. Aziz, V. P. S. Nain, J. S. Carley, W. L. Taylor, and G. T. McGonville, *J. Chem. Phys.*, **70**, 4330 (1979). <sup>c</sup>R. B. Gerber, M. Shapiro, U. Buck, and J. Schlusener, *Phys. Rev. Lett.*, **41**, 236 (1978). <sup>d</sup>R. A. Aziz, P. W. Riley, U. Buck, G. Maneke, J. Schlusener, G. Scoles, and U. Valbusa, *J. Chem. Phys.*, **71**, 2637 (1979). <sup>e</sup>K. M. Smith, A. M. Rulis, G. Scoles, R. A. Aziz, and V. Nain, *J. Chem. Phys.*, **67**, 152 (1977). <sup>f</sup>R. A. Aziz, *High Temp.—High Pressures*, **12**, 565 (1980). <sup>g</sup>C. Y. Ng, Y. T. Lee, and J. A. Barker, *J. Chem. Phys.*, **61**, 1996 (1974). <sup>h</sup>Reference 22. <sup>i</sup>R. A. Aziz and A. van Dalen, *J. Chem. Phys.*, **78**, 2413 (1983). <sup>j</sup>R. A. Aziz and A. van Dalen, *J. Chem. Phys.*, **78**, 2402 (1983). <sup>k</sup>R. A. Aziz, *Mol. Phys.*, **38**, 177 (1979). <sup>l</sup>J. A. Barker, R. O. Watts, J. K. Lee, T. P. Schafer, and Y. T. Lee, *J. Chem. Phys.*, **61**, 3081 (1974). <sup>m</sup>Reference 25. <sup>n</sup>J. Andres, U. Buck, F. Huisken, J. Schlusener, and F. Torello, *J. Chem. Phys.*, **73**, 5620 (1980). <sup>o</sup>R. J. LeRoy and J. S. Carley, *Adv. Chem. Phys.*, **42**, 353 (1980).

TABLE IV: Calculated Potential Parameters<sup>a</sup>

	$\sigma$	$r_m$	$10^4 \epsilon_m$
HeHe	5.00 [0.8]	5.61 [0.0]	0.376 [9.9]
HeNe	5.31 [5.1]	5.93 [5.7]	0.536 [-26]
HeAr	5.87 [0.2]	6.56 [0.0]	1.017 [9.2]
HeKr	6.20 [0.1]	6.92 [0.0]	1.051 [9.8]
HeXe	6.72 [0.4]	7.48 [0.2]	0.940 [5.9]
NeNe	5.61 [8.1]	6.26 [8.3]	0.787 [-42]
NeAr	6.24 [6.8]	6.95 [7.2]	1.385 [-39]
NeKr	6.59 [8.2]	7.33 [8.3]	1.444 [-39]
NeXe	7.18 [11]	7.94 [12]	1.166 [-51]
ArAr	6.37 [0.4]	7.13 [0.4]	4.555 [0.4]
ArKr	6.55 [-0.3]	7.35 [0.3]	5.513 [4.1]
ArXe	6.86 [-0.5]	7.70 [-0.2]	6.384 [7.1]
KrKr	6.79 [0.4]	7.62 [0.6]	5.964 [-5.8]
KrXe	6.93 [-1.9]	7.81 [-1.0]	8.649 [18]
XeXe	7.23 [-1.7]	8.15 [-1.2]	9.129 [2.1]
H <sub>2</sub> He, V <sub>0</sub>	5.61 [-1.1]	6.50 [1.7]	0.488 [-0.2]
H <sub>2</sub> He, V <sub>2</sub>	6.26 [-5.3]	6.95 [-4.5]	0.039 [34]
H <sub>2</sub> Ne, V <sub>0</sub>	5.99 [8.5]	6.71 [7.5]	0.681 [-35]
H <sub>2</sub> Ne, V <sub>2</sub>	6.64 [9.4]	7.34 [8.4]	0.052 [-44]
H <sub>2</sub> Ar, V <sub>0</sub>	6.09 [1.5]	6.87 [1.8]	2.251 [-2.9]
H <sub>2</sub> Ar, V <sub>2</sub>	6.95 [9.4]	7.73 [9.3]	0.132 [-49]

<sup>a</sup>Units and quantities as in Table II. The brackets after each entry represent the percent difference with the corresponding experimental results. V<sub>0</sub> and V<sub>2</sub> are the components in the potential from eq 9. The exchange correction factor for Ne was  $F_x = 0.816$ .

experiment, at both short and long range.

In Figure 8 we plot the experimental and calculated Ne-Ne potential, where it is clear that our calculated potential is much too repulsive. Indeed, in Table IV we see that all interactions involving Ne atoms are too repulsive and show appreciable errors (up to 50% in the well depth). A number of tests were made to ensure that the electronic density for Ne used here was accurate at long range, including performing numerical Hartree-Fock

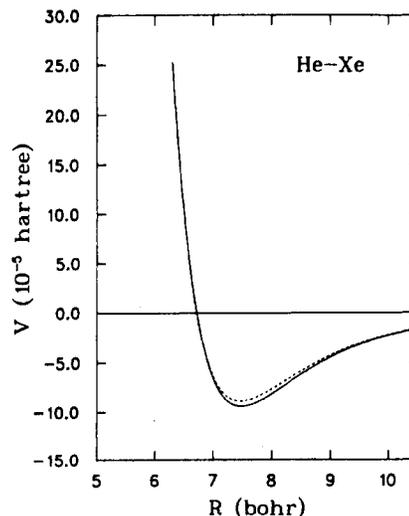


Figure 5. Well region for the He-Xe potential. The dashed line is the experimental result (footnote e Table III) and the solid line the present result.

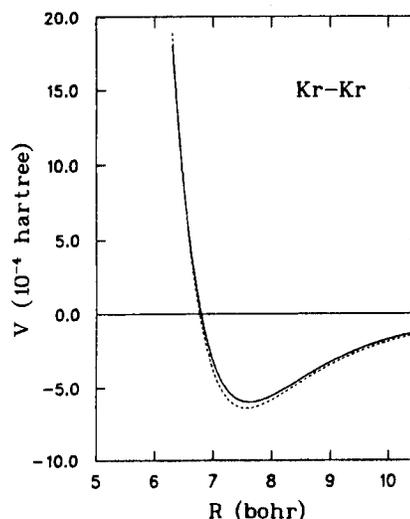


Figure 6. Well region for the Kr-Kr potential. The dashed line is the experimental result (footnote k Table III) and the solid line the present result.

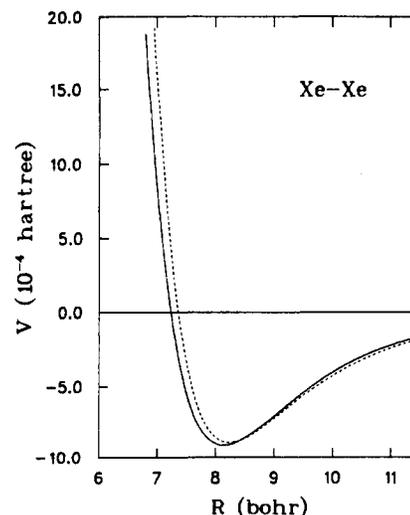
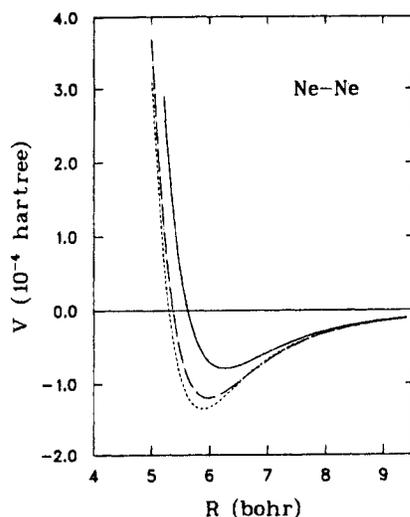


Figure 7. Well region for the Xe-Xe potential. The dashed line is the experimental result (footnote l Table III) and the solid line the present result.

calculations and a self-consistent density functional calculation including correlational terms. In all cases the density at long range

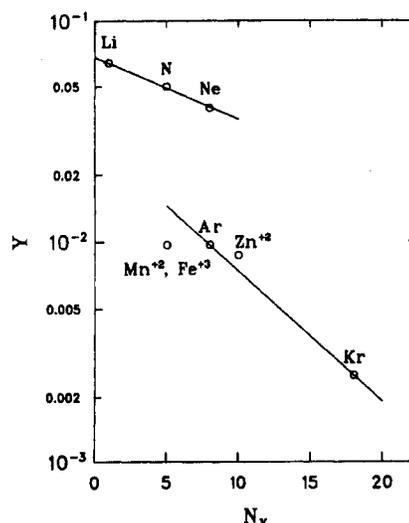


**Figure 8.** Well region for the Ne-Ne potential. The dashed line is the experimental result (footnote *f* Table III). The solid line is the present calculation with the exchange correction factor equal to 0.816 while the dot-dashed line is for a calculation with the exchange correction factor equal to 0.962.

agreed well with that found from the published wave function.<sup>20</sup> Comparison of the Ne results with those of the other calculated interactions leads us to suspect that the MGK model, as applied to pairs containing Ne, is somehow not correct.

The MGK model<sup>3</sup> differs from the earlier versions of the GK model by the introduction of number-of-electron-dependent factors to correct for the nonuniformity of the electronic distributions. While the derivation of the correction factors for the kinetic and correlation energies was straightforward, the exchange energy also included errors due to the self-exchange energy. In their derivation of the exchange correction term  $F_x$ , Waldman and Gordon<sup>3</sup> considered only the self-exchange energy in the valence electrons, as suggested previously by Lloyd and Pugh.<sup>19</sup> They defined, for a series of atoms, the fraction of self-exchange energy per valence electron as  $Y = F/N_v$ , where  $F$  is the ratio of the self-exchange energy in the valence electrons to the total exchange energy and  $N_v$  is the number of electrons in the valence shell (2 for He, 8 for Ne and Ar, and 18 for Kr and Xe). They plotted the logarithm of  $Y$  vs. the total number of electrons,  $N$ , for a series of atoms and approximated the data by a straight line, though there was a great deal of scatter of the points, thus giving a correction factor that depended on both  $N$  and  $N_v$ . However, plotting the  $Y$  values from the Waldman-Gordon paper (Figure 2 of ref 3) vs.  $N_v$  instead of  $N$  (Figure 9) shows what looks like a definite split in the curves. The values for atoms in the first row clearly fall on a straight line. While there is scatter in the other points, a straight line drawn between the points for Ar and Kr gives a total fit that is better than that found by Waldman and Gordon. Clearly, a more thorough investigation of the exchange term is in order. Lloyd and Pugh<sup>19</sup> have suggested that only the total number of valence electrons should be considered in deriving the correction factor for interacting systems. We do not feel this is correct (see Figure 9) as it fails to correct for differences in size and uniformity of the electron distribution. For the purposes of this paper, however, we choose to set the Ne-Ne exchange correction factor (for 16 valence electrons) equal to that for Ar-Ar ( $F_x = 0.962$  instead of 0.816) and to define the exchange factor as depending only on  $N_v$ . With this choice of exchange correction factor for Ne-Ne, the factors for Ne with other atoms are the same as for Ar.

In Figure 8 we have plotted the Ne-Ne potential calculated with  $F_x = 0.962$ . There is clearly great improvement of the potential over that calculated with the smaller correction factor. We see in Table V that overall the agreement for those systems involving Ne atoms is greatly improved by the change in correction factor, though they are not as good as the other results, with the potentials still being uniformly too repulsive.



**Figure 9.** Correction factor for the exchange energy vs. number of valence electrons. The data are from ref 3 and defined as discussed in text.

**TABLE V: Revised Parameters for Ne Interactions<sup>a</sup>**

	$\sigma$	$r_m$	$10^4 \epsilon_m$
HeNe	5.18 [2.5]	5.79 [3.1]	0.670 [-7.4]
NeNe	5.36 [3.2]	5.97 [3.3]	1.197 [-12]
NeAr	6.08 [4.2]	6.78 [4.5]	1.747 [-23]
NeKr	6.42 [5.5]	7.15 [3.0]	1.825 [-23]
NeXe	6.96 [7.7]	7.73 [9.1]	1.604 [-32]
NeH <sub>2</sub> , $V_0$	5.84 [5.8]	6.54 [4.8]	0.855 [-18]
NeH <sub>2</sub> , $V_2$	6.50 [6.6]	7.19 [6.2]	0.063 [-32]

<sup>a</sup>Notation and units as in Table IV. The exchange correction factor for Ne was  $F_x = 0.962$ .

As discussed by Waldman and Gordon,<sup>3</sup> the repulsive wall regions of the potentials are not as sensitive to the choice of correction factors as are the well regions, and inclusion of the scaling factors does not greatly alter the excellent agreement with experiment on the repulsive wall found in the original model.<sup>1</sup> Thus, our relatively small changes in these factors for unlike interactions should produce modest changes in the repulsive wall. The reader is referred to the earlier work<sup>3</sup> for examples of the potentials in this region.

**B. Atom-Molecule Results.** The dispersion energy for atom-molecule systems is given by

$$V_d(r, \theta) = -[D_0(r) + D_2(r) P_2(\cos \theta)] \quad (7)$$

where

$$D_i(r) = \left\{ \frac{C_6^i}{r^6} + \frac{C_8^i}{r^8} + \frac{C_{10}^i}{r^{10}} \right\} \quad (8)$$

and  $P_2(\cos \theta)$  is the second Legendre function. For atom-homonuclear diatomic systems with small anisotropy, the total potential can be written as

$$V(r, \theta) \approx V_0(r) + V_2(r) P_2(\cos \theta) \quad (9)$$

where

$$V_0(r) \approx \frac{1}{3}[V(r, 0) + 2V(r, 90)]$$

$$V_2(r) \approx \frac{2}{3}[V(r, 0) - V(r, 90)]$$

We have applied the present model to H<sub>2</sub>-He, -Ne, and -Ar using the dispersion coefficients in Table II. We calculated the total potential at  $\theta = 0$  and  $90^\circ$  by using the dispersion energy (eq 7) and GK potential appropriate for that angle. The position of the minimum of the potential,  $r_m$ , is then found self-consistently in the same manner as for atom-atom potentials. The results for the H<sub>2</sub>-He and H<sub>2</sub>-Ar systems are quite good and better than the results using the electron-gas-Drude model;<sup>8</sup> however, there

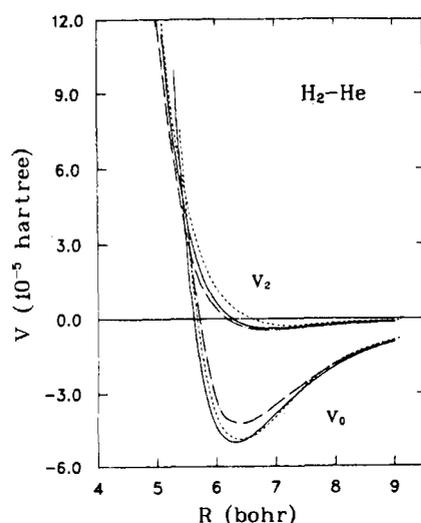


Figure 10.  $V_0(r)$  and  $V_2(R)$  for He-H<sub>2</sub>. The dashed lines are the experimental results from ref 25 and the solid lines are the present results. The chain dotted lines are from the theoretical calculation of ref 27.

is appreciable error in  $V_2$ , for both H<sub>2</sub>-He and H<sub>2</sub>-Ar. These potentials are very flat and so small errors in shape can make large errors in well parameters. The  $V_2$  potentials are also very sensitive to changes in the anisotropy parameters for the dispersion energy (see the second paper in ref 12). We have not examined how changes in these parameters affect our potentials. Another difficulty is deciding what experimental or theoretical data with which to compare and, indeed, the accuracy of such data. For He-H<sub>2</sub>, we have compared our results to the potentials of Shafer and Gordon,<sup>25</sup> which were based on earlier work on  $V_0$  by Gengenbach and Hahn.<sup>26</sup> Our calculated potential is compared with the Shafer and Gordon result in Figure 10. Some<sup>13,16</sup> have argued that the accurate theoretical results of Meyer et al.<sup>27</sup> should be used. Meyer et al. found the following for  $V_0$ :  $r_m = 6.43$  [1.1],  $\epsilon_m = 4.22 \times 10^{-5}$  [16], and  $\sigma = 5.71$  [-1.8], with the percent difference between the present results and their results given in brackets. For  $V_2$ , they obtain the following:  $r_m = 6.85$  [1.5];  $\epsilon_m = 4.4 \times 10^{-16}$  [-1.1];  $\sigma = 6.14$  [1.8]. Comparison with Table IV shows that our results for  $V_0$  agree much better with the experimental results<sup>25,26</sup> while our results for  $V_2$  agree better with the theoretical calculations. The theoretical results are shown in Figure 10. It is very difficult to say exactly which is the best comparison. In Figure 11 we compare our theoretical results for Ar-H<sub>2</sub> with the experimental curves. In general, the agreement is quite satisfactory considering the simplicity of the model and ease of the calculations.

For H<sub>2</sub>-Ne, use of the Waldman-Gordon correction terms for the Ne-Ne interaction gives a potential that is too repulsive (Table IV). The results are improved (Table V) by taking the Ne-Ne correction factor to be 0.962; however, they still are not as good as for the other systems.

#### IV. Discussion

Even with the simple damping function used here, very close agreement between experiment and theory was obtained. Overall, neglecting Ne interactions, the present results are as good as or better than the results using similar methods.<sup>12-15</sup> The advantage of the present method is that the short-range potential is obtained with the Gordon-Kim model, which takes orders of magnitude less computer time than the Hartree-Fock SCF calculations upon which the other methods were based. Thus, the present method can be easily applied to other, more complicated, systems, such as those involving polyatomic molecules. One disadvantage to the present method is that the GK model is designed to study only the interactions between closed-shell atoms and molecules.

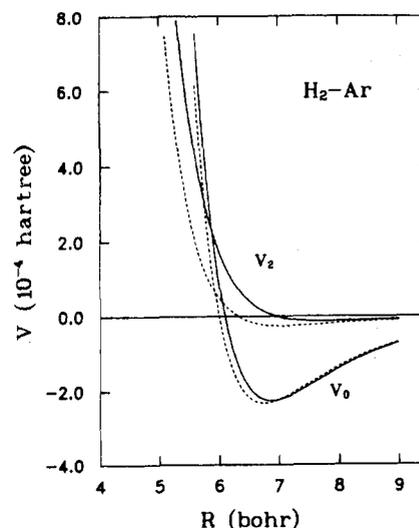


Figure 11.  $V_0(R)$  and  $V_2(R)$  for Ar-H<sub>2</sub>. The dashed lines are the experimental results (footnote *o* Table III) and the solid lines are the present results.

The present method was designed to give improved results for the well regions of intermolecular interactions. As noted earlier, the repulsive wall regions as calculated with the MGK model are in reasonably good agreement with experiment. However, in the present study, we have set the correlational energy component ( $E_c$  in eq 2) to zero. This term makes a small negative contribution to the total potential that is assumed to be included in the dispersion energies. Because of the form of the damping function used here, the magnitude of the total dispersion energy ( $f(x) V_d(r)$ ) reaches a maximum at distances less than the potential minimum (for Ar-Ar it is about at  $x = 0.5$ ) and then goes to zero for smaller distances. Comparing the damped dispersion energy,  $V_{disp}$ , with the MGK correlational energy ( $E_c$ ) calculated with the correction factor of ref 3 for Ar-Ar, we find that at long range,  $V_{disp}$  is much larger in magnitude, as expected. For  $0.5 \leq x \leq 0.7$ ,  $E_c$  and  $V_{disp}$  are roughly comparable (within 10-40% of each other), and since they represent only about 3% (at  $x = 0.95$ ) to 10% (at  $x = 0.7$ ) of the total short-range potential, the net difference of using one term or the other is quite small. At small separations ( $x \leq 0.5$ ), where  $V_{disp}$  is going to zero,  $E_c$  represents only about 1% of the total short-range potential so can be neglected without much error. Thus, use of the damping function will not greatly affect the total potential in the repulsive well region, so our calculation potentials should still be a reasonable representation of the true potential.

The rather poor results for systems involving Ne atoms is puzzling and a bit disturbing. The results are improved by increasing the exchange correction factor, but they still are not as good as for the other systems. That there may be something inherently wrong with the model is indicated by the fact that interactions involving Ne atoms are uniformly too repulsive. These results are similar to those found recently by Muhlhausen and Gordon<sup>28</sup> when applying the MGK model to ionic crystals. Examination of their Figure 1 shows that the calculated lattice parameters of crystals involving Na<sup>+</sup>, Mg<sup>2+</sup>, and F<sup>-</sup> ions, which are isoelectronic with Ne, are almost uniformly too large, while the errors for crystals involving other ions are randomly distributed. For NaF, using the MGK correction factor for Ne-Ne, they found lattice parameters that were 2.6% too large. Using a similar program,<sup>4,10</sup> we have found that, by using the Ar-Ar factor (0.962), the error is reduced to 1.3%. Thus, it seems that further study of the exchange correction factor in the MGK model is in order.

#### V. Summary

We have presented a very simple model for including dispersion interactions up to  $r^{-10}$  with Gordon-Kim short-range potentials

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to give accurate representations of the pair potentials between closed-shell atoms and molecules. While problems remain in dealing with systems involving second-row atoms, the simplicity of the model encourages us to feel that it could play a useful role in calculating pair interactions between quite complicated systems.

*Note Added in Proof.* After submission of this article, Tang and Toennies<sup>29</sup> published a new model of a universal damping function for the dispersion interactions. The new model is similar to their previous one<sup>12</sup> but is easier to use in that the only parameter in their function is the exponent in a Born-Mayer fit to the repulsive, short-range interactions. However, they found that using SCF short-range potentials with their function gave po-

tentials that are too soft. In practice, they chose the parameters in the repulsive part of the potential to fit the experimental data. It would be interesting to use their damping function with a Born-Mayer fit to MGK short-range energies.

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## Interfacial Electron-Transfer Equilibria and Flat-Band Potentials of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> Colloids Studied by Pulse Radiolysis

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The kinetics and equilibria of electron transfer between methylviologen cation radicals and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> or TiO<sub>2</sub> colloidal particles were studied with the pulse-radiolysis technique. The rates of electron transfer to both colloids are lower than those predicted for a diffusion-controlled reaction. For higher pHs (TiO<sub>2</sub>, pH > 2;  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, pH > 9) the established equilibrium  $MV^+ \rightleftharpoons MV^{2+} + (e^-)_{coll}$  is strongly influenced by the MV<sup>2+</sup> concentration and pH. The MV<sup>+</sup> equilibrium concentration can be exploited to derive the flat-band potential of the semiconductor colloids. The method for determining the flat-band potential of the particles is independent of whether the injected electrons are free or trapped, and whether the electrons raise the bulk Fermi level toward the conduction band or just produce a space charge. The flat-band potentials for both colloids appear to be somewhat more negative (-0.1 to -0.2 V) than the corresponding single-crystal electrodes. Also, the flat-band potentials become slightly more negative with increasing radiation dose (initial MV<sup>+</sup> concentration). The effect of absorbed radiation dose is explained by the corresponding changes in the ratio of oxidized to reduced forms of the redox couple, which in turn changes the adsorbed ionic charge on the semiconductor surface. For colloidal particles of TiO<sub>2</sub> stabilized by poly(vinyl alcohol) (PVA), the flat-band potentials were almost the same as those for PVA-free TiO<sub>2</sub> sols. The decrease of particle diameter from 800 to 70 Å does not affect the value of the flat-band potentials for TiO<sub>2</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> colloids.

### Introduction

In recent years, attention has been focused on the use of particulate semiconductors which behave as microelectrodes for photoelectrochemical reactions, such as the photochemical cleavage of water and the photoreduction of CO<sub>2</sub>.<sup>2,3</sup> Semiconductor particles have small size, and their photoelectrochemical properties may not be the same as those of large, single-crystal electrodes.

The particle diameter can be smaller than the thickness of the space charge layer and in that case the details of charge separation may not be the same as in a compact semiconductor electrode.<sup>3,4</sup> The particles also have a large surface-to-bulk ratio, and surface states may therefore be especially important in the interpretation of the photoelectrochemical behavior of colloids.

Information on the photoelectrochemical properties of semiconductors in particle form can be obtained by studying interfacial charge transfer reactions in microheterogeneous systems. In order to make a connection between the energy levels of the electrolyte and those of the semiconductor particles, it is important to know their flat-band potential,  $E_{fb}$ . The flat-band potential is a measure of the reducing power of semiconductor materials, and it is related to the electron affinity of the semiconductor and the charge density at the surface. Previous work on the reduction of methyl viologen (MV<sup>2+</sup>) by conduction band electrons produced via laser excitation of TiO<sub>2</sub> colloids (Grätzel et al.)<sup>5</sup> showed that the Fermi level of TiO<sub>2</sub> in the sol at pH 2-3 is in equilibrium with the redox potential of the MV<sup>2+</sup>/MV<sup>+</sup> couple, and this potential was taken to be the flat-band potential.

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