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# Interaction potentials for alkali ion–rare gas and halogen ion–rare gas systems

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The Tang–Toennies model [J. Chem. Phys. **80**, 3725 (1984)] has been modified to predict the potentials for ion–atom systems. First order SCF energies are used to describe the repulsive potential. The long range second order induction and dispersion potential terms up to  $R^{-10}$  are either taken from *ab initio* calculations or estimated and each term is appropriately damped. The potentials for  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{F}^-$ , and  $\text{Cl}^-$  interacting with He, Ne, and Ar are found to agree well with both theoretical and experimental data within the expected errors. For comparison with the model new *ab initio* calculations have been performed for  $\text{Na}^+$ –Ar and the results are in excellent agreement with the model predictions ( $< 10\%$ ).

## I. INTRODUCTION

The diffusion and mobility of ions is an important process for understanding discharges, plasmas, and upper atmosphere physics.<sup>1</sup> Despite over 75 years of study, the potentials governing the elementary collision processes are still not known with an accuracy comparable to that recently achieved for the rare gas–atom interactions.<sup>2,3</sup> The first theories of ion–atom potentials probably go back to Langevin<sup>4</sup> (1908) and Margenau<sup>5</sup> (1941). Since then a number of different theoretical approximations have been tried including the electron-gas model<sup>6–9</sup> pseudopotential methods<sup>10</sup> and *ab initio* calculations.<sup>11–15</sup> In the present paper we have modified the model of Tang and Toennies,<sup>16</sup> which has been used successfully to describe atom–atom potentials, to deal with ion–atom systems. In the course of this work, two related studies have appeared by Siska<sup>17</sup> and Patil,<sup>18</sup> using similar models but with fewer potential terms and with results for only a few of the systems treated here.

Two experimental developments have made it worthwhile to attempt a more refined theoretical determination of the ion–atom potentials. First of all sophisticated procedures have been developed for analyzing gaseous ion transport data. With a minimum of assumptions these procedures make it possible to invert measured ion mobilities and diffusion coefficients to determine directly the potential energies as a function of internuclear distance.<sup>19,20</sup> In addition molecular beam scattering experiments have become increasingly successful in providing critical data on these systems.<sup>21,22</sup> The interpretation of this cross section data is not nearly as straightforward, however, as in the case of atom–atom potentials because of the much higher energies which are required to avoid space and surface-charge problems. Thus for these experimental reasons quantum interference effects, which provide the most precise measurements of the potential range parameters, have with a few exceptions not been observed.<sup>23,24</sup> Other sources of potential information available for atom–atom potentials, such as crystallographic lat-

tice spacings and compressibilities are also not available for ion–atom partners. A new source of data on these potentials may become available from studies of the scattering of rare gas atoms from alkali–halide crystals. One recent analysis suggests that the additive potential appears to be a good approximation.<sup>25</sup>

The present paper is organized as follows. The next section describes the potential model and how it is modified to take account of interactions specific to ions. The following section describes the procedures used to calculate the first order self-consistent field (SCF) repulsive potentials. The sources of information on the long range potential parameters are surveyed and combining rules are used to estimate those parameters not available in the literature. The results for the interactions with the positive ions  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and the target rare gases He, Ne, and Ar are then presented. Next the problems in estimating long range parameters for the negative halogen ions are discussed and suggested potentials for  $\text{F}^-$ ,  $\text{Cl}^-$  with He, Ne, and Ar are presented. The paper closes with a discussion of the results and some comparisons with other potentials.

## II. THE MODIFIED POTENTIAL MODEL

First we note that the potentials for ion–atom interactions are dominated at short range by exchange and coulomb repulsion and in the long range region by second order classical electrostatic induction interactions. For most systems the relative contribution from quantum mechanical dispersion forces is small. This suggests that for these systems second order SCF calculations with only a small correction for dispersion forces would provide already a good description of the potentials. Nevertheless, few accurate second order SCF calculations have been reported.<sup>12–14</sup>

Since the second order induction forces can be well described classically we modify our previous potential model to include the second order effects separately from the SCF repulsion. The full SCF energy can be decomposed into a

first order term  $E_{\text{SCF}}^{(1)}$  and the remaining SCF energy  $E_{\text{SCF}}^{(r)}$ :

$$E_{\text{SCF}} = E_{\text{SCF}}^{(1)} + E_{\text{SCF}}^{(r)}. \quad (1)$$

Böhm and Ahlrichs<sup>26</sup> have pointed out that in the region of chemical importance the short range repulsion is dominated by  $E_{\text{SCF}}^{(1)}$ , which can be accurately approximated by a Born–Mayer  $A \exp(-bR)$  function. Thus we assume that the full potential can be considered to be composed of the sum of the following terms:

$$V(R) = E_{\text{SCF}}^{(1)} + E_{\text{induction}}^{(2)} + E_{\text{dispersion}}^{(2)} + E_{\text{intra}} + E_{\text{ex disp}} + E_{\text{ex ind}} + \text{higher order terms}, \quad (2)$$

where the second term is the classical expansion of the second order induction potential<sup>27</sup> and the third term accounts for the quantum mechanical dispersion interaction. The fourth term in Eq. (2) takes account of the change of the interatomic correlation energy of each of the partners as a result of the intermolecular interaction. The fifth and sixth terms account for a coupling between the second order terms and chemical exchange.<sup>16,28</sup>

The strength parameters of  $E_{\text{induction}}^{(2)}$  and  $E_{\text{dispersion}}^{(2)}$  can be either calculated or estimated from known atomic properties of the individual partners. The damping of the individual terms in each of the expansions can be accounted for by using the simple analytic expression obtained by Tang and Toennies.<sup>16</sup> This expression for the damping has recently been confirmed also to be correct for treating the induction forces by a simple model calculation for  $\text{H}_2^+$ .<sup>29</sup> Very little is known about the last three terms. Conventional *ab initio* quantum chemical theory has so far not been successful in providing estimates for these terms for arbitrary systems. Some information is available on  $E_{\text{intra}}$  for a few selected systems.<sup>30</sup> Since the definition of  $E_{\text{intra}}$  is still open to debate<sup>31</sup> we assume that  $E_{\text{intra}}$  can be absorbed in  $E_{\text{ex ind}}$  and  $E_{\text{ex disp}}$ . The latter term including  $E_{\text{intra}}$  is here assumed to be given by an empirical relationship

$$E_{\text{ex disp}} = 0.17 A \exp(-bR) \quad (3)$$

recently deduced from an analysis of  $\text{H}_2^+ \Sigma$  and a large number of rare gas–rare gas atom systems and several other van der Waals systems.<sup>16</sup> For  $\text{H}_2^+$  it has recently been possible to derive an expression for  $E_{\text{ex ind}}$  with the result<sup>29,32</sup>

$$E_{\text{ex ind}} = 0.14 A \exp(-bR). \quad (4)$$

Both exchange terms can thus be accounted for by multiplying  $E_{\text{SCF}}^{(1)}$  by a factor 1.31.

With these assumptions, the potential model reduces to

$$V = A_{\text{eff}} \exp[-b^{(1)}R] - f_4(R)D_4/R^4 - f_6(R)D_6/R^6 - f_8(R)D_8/R^8 - f_{10}(R)D_{10}/R^{10}, \quad (5)$$

where

$$\begin{aligned} A_{\text{eff}} &= 1.31 A_{\text{SCF}}^{(1)}, \\ D_4 &= \frac{1}{2} \alpha_1(\text{atom}), \\ D_6 &= \frac{1}{2} \alpha_2(\text{atom}) + C_6(\text{atom-ion}), \\ D_8 &= \frac{1}{2} \alpha_3(\text{atom}) + C_8(\text{atom-ion}), \\ D_{10} &= \frac{1}{2} \alpha_4(\text{atom}) + C_{10}(\text{atom-ion}), \end{aligned}$$

$$f_n(R) = 1 - \exp(-b^{(1)}R) \sum_{k=0}^n \frac{[b^{(1)}R]^k}{k!},$$

where  $A_{\text{SCF}}^{(1)}$  and  $b^{(1)}$  are the strength and range parameters from a Born–Mayer fit of the first order SCF calculations,  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ , and  $\alpha_4$  are the static dipole, quadrupole, octupole, and hexadecapole polarizabilities of the atoms and  $C_6$ ,  $C_8$ , and  $C_{10}$  are the first three terms in the usual dispersion expansion. Higher order terms can be safely neglected since their contributions are estimated to be less than 2%.

### III. FIRST ORDER SCF REPULSIVE POTENTIALS

The first order SCF repulsive parameters have been calculated in a straightforward way. Let  $\Psi_A$  and  $\Psi_B$  denote the SCF wave functions of isolated atoms or atomic ions and  $\Psi_{AB}(R)$  the corresponding antisymmetrized product function for the system  $A \cdots B$  at distance  $R$ ,

$$\Psi_{AB} = A[\Psi_A \Psi_B]. \quad (6)$$

The first order SCF interaction energy  $E_{\text{SCF}}$  is then simply obtained from

$$E_{\text{SCF}}^{(1)} = \langle \Psi_{AB} | H | \Psi_{AB} \rangle / \langle \Psi_{AB} | \Psi_{AB} \rangle - E_{\text{SCF}}(A) - E_{\text{SCF}}(B). \quad (7)$$

The first term on the right-hand side is the first order SCF energy of  $A \cdots B$  and the remaining terms denote the SCF energies of the isolated systems. Since we are dealing with closed shell systems the evaluation of  $E_{\text{SCF}}^{(1)}$  is technically very simple.<sup>26</sup> The reliable evaluation of  $E_{\text{SCF}}^{(1)}$  is in fact relatively easy since it involves only the occupied SCF orbitals of  $A$  and  $B$ , and no problems arise from basis set superposition errors (BSSE).<sup>33</sup> BSSE is a serious problem in SCF and especially CI-type calculations of the (super)system  $A \cdots B$  since basis functions on  $A$  always serve to improve the description of  $B$  (and vice versa). This leads to a lowering of total energies as a consequence of the necessarily incomplete basis sets which have to be used.

In the present calculations we have employed contracted Gaussian basis sets obtained from Huzinaga's tables.<sup>34</sup> The following basis sets were used

He	(8)/[5],
Li <sup>+</sup>	(9)/[6],
F <sup>-</sup>	(11,7)/[7,4] plus diffuse $p$ : $\eta = 0.074$ ,
Ne, Na <sup>+</sup>	(11,7)/[7,4],
Cl <sup>-</sup>	(12,9)/[8,6] plus diffuse $p$ : $\eta = 0.05$ ,
Ar	(12,9)/[8,6],
K <sup>+</sup>	(13,9)/[9,6].

The  $s$  basis of  $\text{K}^+$  was obtained from the  $14s$  basis of the neutral atom, the two most diffuse  $s$  functions, describing the  $4s$  atomic orbital, were deleted and a function with  $\eta = 0.1$  added. The contraction always involved the steepest Gaussians with contraction coefficients taken from the  $1s$  or  $2p$  SCF atomic orbitals of the corresponding atomic calculation, which makes the above characterization unambiguous.

For each of the systems the potential energies were calculated at five to eight different internuclear distances  $R$  and the results were least-square fitted to a Born–Mayer function. The resulting values for  $A$  and  $b$  are listed in Table I, where they are compared with previous calculations where

TABLE I. Born-Mayer parameters (in a.u.) obtained from a best fit of first order SCF calculations. Where available other published values are shown for comparison.

	<i>A</i>	<i>b</i>	Standard deviation $\sigma^a$
Li <sup>+</sup> -He	23.92	2.694	$9.1 \times 10^{-6}$
	33.167 <sup>b</sup>	2.717 <sup>b</sup>	...
	25.610 <sup>b</sup>	2.670 <sup>b</sup>	...
	43.909 <sup>c</sup>	2.8066 <sup>c</sup>	...
-Ne	67.31	2.699	$6.9 \times 10^{-5}$
-Ar	118.6	2.264	$3.6 \times 10^{-5}$
Na <sup>+</sup> -He	57.1	2.573	$3.8 \times 10^{-5}$
	35.610 <sup>b</sup>	2.350 <sup>c</sup>	...
	36.121 <sup>b</sup>	2.337 <sup>c</sup>	...
	254.0	2.6968	$1.2 \times 10^{-5}$
-Ne	389.8	2.2857	$1.1 \times 10^{-5}$
-Ar			
K <sup>+</sup> -He	129.2	2.3317	$2.6 \times 10^{-5}$
	488.1	2.4281	$2.2 \times 10^{-5}$
	696.4	2.1028	$2.6 \times 10^{-5}$
F <sup>-</sup> -He	25.21	1.997	$2.0 \times 10^{-5}$
	9.249 <sup>c</sup>	1.7392 <sup>c</sup>	...
	162.0 <sup>d</sup>	2.346 <sup>d</sup>	...
	28.48	1.8219	$3.2 \times 10^{-5}$
-Ne	52.95	1.7119	$2.3 \times 10^{-5}$
-Ar			
Cl <sup>-</sup> -He	21.37	1.5797	$8.6 \times 10^{-5}$
	31.96	1.5741	$1.8 \times 10^{-5}$
	90.18	1.5529	$4.1 \times 10^{-5}$

<sup>a</sup> Defined by  $\sigma^2 = 1/N \sum_{i=1}^N (\Delta E_i)^2$ , where  $\Delta E_i$  is the difference between the energies at the calculated points and those for the best-fit Born-Mayer function.

<sup>b</sup> These values were reported in Ref. 12 and were obtained by fitting the reported SCF calculation to the simple expression  $A \exp(-bR) + A_2 R^{-4}$ . Since this formula does not account for the dispersion potential nor the damping the resulting parameters cannot be compared directly.

<sup>c</sup> P. W. Fowler and J. M. Hutson, Ref. 35. Note that these results were obtained from full Hartree-Fock calculations, which were corrected in a different way than used here for the induction potential. These values are therefore similar but cannot be compared directly with the present results.

<sup>d</sup> V. Celli *et al.*, Ref. 25. These values were obtained from a fit of the same data points with special emphasis on the long range region. The results for  $R_0$ ,  $R_m$ , and  $\epsilon$  (Table VIII) with these parameters are nearly the same, however.

available. Also listed are the root-mean values of the sum of the squared deviations for all points. The small values indicate that they could all be well fitted by an exponential. A close examination of the data points revealed however somewhat larger deviations from the best-fit exponential for certain systems at the equilibrium distances determined in this study. These deviations were typically less than  $\pm 2\%$  except for Cl<sup>-</sup>-He ( $-12\%$ ), K<sup>+</sup>-He ( $-9\%$ ) and Cl<sup>-</sup>-Ne ( $-5\%$ ). Since the repulsive potential is more than compensated for by the attractive potential the resulting error in the total potential is less than one-half this amount.

With the availability of these data we can study the effect of the different charge states by comparing the potentials for the isoelectronic systems He-He and Li<sup>+</sup>-He; F<sup>-</sup>-Ne, Ne<sup>-</sup>-Ne and Na<sup>+</sup>-Ne; and finally Cl<sup>-</sup>-Ar, Ar-Ar, and K<sup>+</sup>-Ar. The three sets of potentials are shown in Figs. 1, 2, and 3. Here we have taken the effective Born-Mayer parameters for the rare gas dimers from a recent analysis of experi-

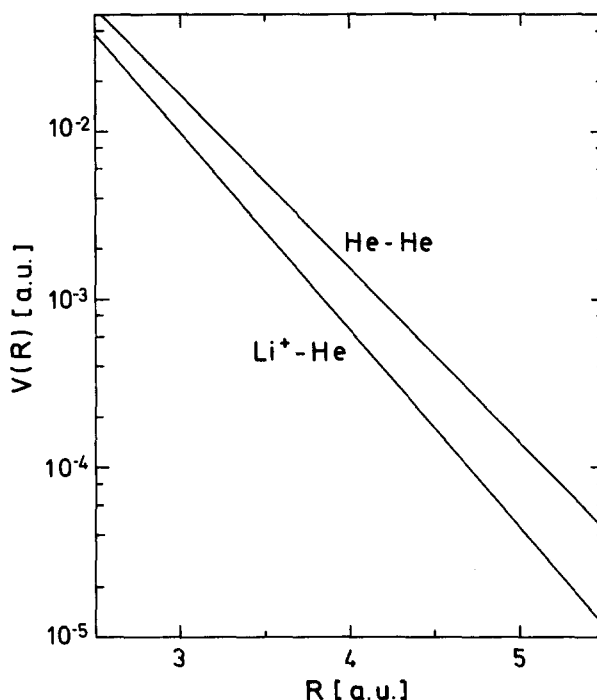


FIG. 1. Comparison of effective Born-Mayer repulsive potentials for the isoelectronic systems He-He and Li<sup>+</sup>-He. The He-He data have been taken from a recent fit of exponential data based on the Tang-Toennies potential model. The Li<sup>+</sup>-He data are from the first order SCF calculations reported here but multiplied by a factor 1.31.

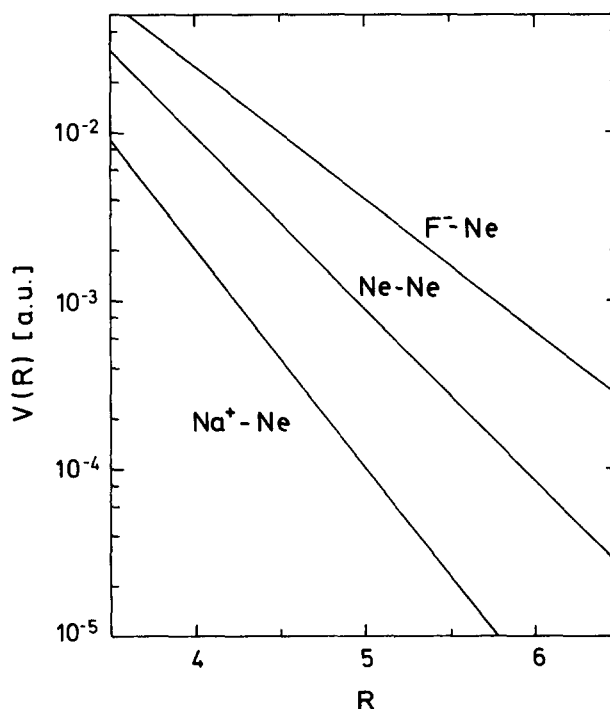


FIG. 2. Comparison of effective Born-Mayer repulsive potentials for the isoelectronic systems Ne-Ne, Na<sup>+</sup>-Ne, and F<sup>-</sup>-Ne. The Ne-Ne data have been taken from a recent fit of experimental data based on the Tang-Toennies potential model. The Na<sup>+</sup>-Ne and F<sup>-</sup>-Ne data are from the first order SCF calculations reported here but multiplied by a factor 1.31.

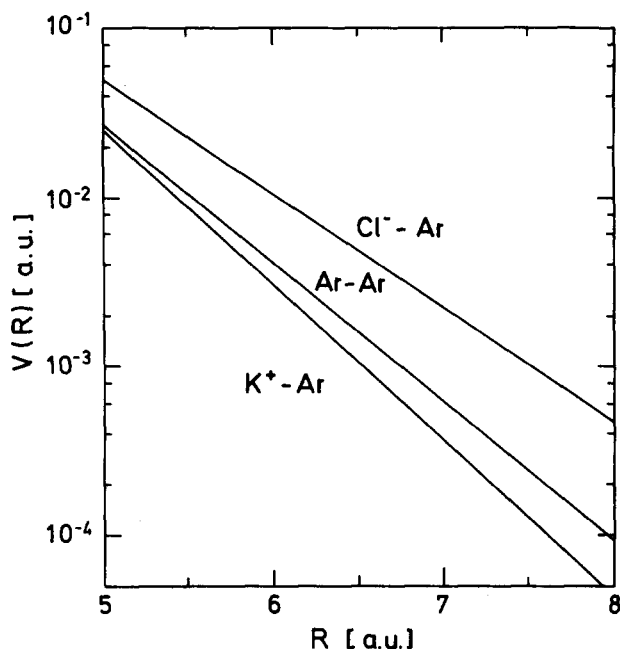


FIG. 3. Comparison of effective Born-Mayer repulsive potential for isoelectronic systems Ar-Ar,  $K^+$ -Ar, and  $Cl^-$ -Ar. The Ar-Ar data have been taken from a recent fit of experimental data based on the Tang-Toennies potential model. The  $K^+$ -Ar and  $Cl^-$ -Ar data are from the first order SCF calculations reported here but multiplied by a factor 1.31.

mental potential data based on the Tang-Toennies potential model.<sup>3</sup> In order to compare with these effective potentials we have multiplied all the ion-atom potentials by the factor 1.31 discussed above.

#### IV. INDUCTION AND DISPERSION COEFFICIENTS

##### A. The induction potential

The attractive potential for the ion-atom systems are largely dominated by the attractive induction potentials. They depend only on the dipole  $\alpha_1$ , quadrupole  $\alpha_2$ , octupole  $\alpha_3$ , and hexadecapole  $\alpha_4$  polarizabilities of the rare gas atoms. Fortunately these polarizabilities are well known from theoretical studies with an accuracy of several percent. The values used are summarized in Table II, which also includes values of the corresponding average electronic excitation energies.

##### B. Dispersion coefficients between positive ions and rare gas atoms

In comparison to the induction potentials the dispersion potential contributes less than 25% to the potential in the

well region and even less outside of the immediate well region. Our knowledge of the dispersion coefficients for the ion-rare gas interactions is much less satisfactory than for the rare gas-rare gas interactions.

Since the polarizabilities of the rare gases and positive ions and the dispersion constants for the alkali ions are known we can use accurate combining rules to calculate  $C_6$ ,  $C_8$ ,  $C_{10}$  between the positive ions and the rare gas atoms. These combining rules are extensively discussed in a recent investigation<sup>3</sup> and the reader is referred to Eqs. (9a)–(9c) and (10a)–(10c) of this publication. The necessary rare gas input data is the same as in Table II. The available dispersion constants and polarizabilities and average electronic excitation energies of the positive ions are summarized in Table III. The  $C_6$ ,  $C_8$ , and  $C_{10}$  coefficients from the combining rules are compared with the recent theoretical calculations of Bartoletti<sup>39</sup> in Table IV. It is gratifying to see that for all systems the agreement between the combining rule estimates and the *ab initio* calculations for  $C_6$  is better than about 3%, which is of the order of the estimated accuracy of the combining rules, and thereby confirms the accuracy of these rules for ion-atom interactions. The agreement for the higher order dispersion coefficients is not as good but in view of the uncertainties in the input data and theories used is regarded as satisfactory.

##### C. Dispersion coefficients between negative ions and rare gas atoms

###### 1. Estimates based on polarizabilities

To estimate the dispersion coefficients for the negative ion-rare gas atom interactions we must first establish values for the  $C_6$  and  $C_8$  constants for the  $F^-$ - $F^-$  and  $Cl^-$ - $Cl^-$  interactions. Then we can use the same combining rules used previously to estimate the ion-atom coefficients.

To estimate the negative ion interactions we use the data for the negative ion polarizabilities for the induction potentials and effective number of electrons involved in the interaction collected in Table V for the dispersion potentials. The polarizability data is from McEachran *et al.*<sup>45</sup> More recent calculations for both  $F^-$  and  $Cl^-$  yield factor two larger values for the dipole polarizability.<sup>46,47</sup> However, since the values of McEachran *et al.* are more consistent with other literature values we have adopted their values. The effective number of electrons for  $F^-$  was obtained from the Slater-Kirkwood formula<sup>48</sup>

$$C_6 = \frac{3}{2} \alpha_1^{3/2} N_{\text{eff}}^{1/2}, \quad (8)$$

using the value of  $C_6 = 46.3$  a.u. obtained by Donath<sup>44</sup> from a HF-Cl calculation for  $F^-$ - $F^-$ . For  $Cl^-$  a value of  $C_6$  is

TABLE II. Summary of theoretical and estimated dispersion coefficients, polarizabilities, and average excitation energies  $\Omega_i$  for the rare gases taken from Ref. 3. All values are in a.u.

	$C_6$	$C_8$	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_4$	$\Omega_1$	$\Omega_2$	$\Omega_3$
He-He <sup>a</sup>	1.46	14.1	1.38	2.44	10.6	80	1.019	1.228	1.356
Ne-Ne <sup>a</sup>	6.87	75.0	2.66	6.42	30.4	267	1.295	1.069	1.108
Ar-Ar <sup>a</sup>	67.20	1480.0	11.10	52.4	490	6190	0.727	0.636	0.672

<sup>a</sup> All entries taken from Table I of Ref. 3, except for  $\alpha_4$ , which is from Ref. 36.

TABLE III. Summary of dispersion coefficients, polarizabilities, and average excitation energies for positive ions.

	$C_6$	$C_8$	$C(1,3)$	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\Omega_1^e$	$\Omega_2^f$	$\Omega_3^g$
$\text{Li}^+-\text{Li}^+$	0.078 <sup>a</sup>	0.256 <sup>c</sup>	0.375 <sup>c</sup>	0.192 <sup>a</sup>	0.114 <sup>b</sup>	0.173 <sup>c</sup>	2.821	3.420	3.765
$\text{Na}^+-\text{Na}^+$	1.61 <sup>d</sup>	14.4 <sup>c</sup>	43.5 <sup>c</sup>	1.00 <sup>d</sup>	1.798 <sup>c</sup>	5.982 <sup>c</sup>	2.146	2.120	2.013
$\text{K}^+-\text{K}^+$	23.3 <sup>d</sup>	42.3 <sup>c</sup>	2560 <sup>c</sup>	5.47 <sup>d</sup>	17.8 <sup>c</sup>	122 <sup>c</sup>	1.038	1.251	1.289

<sup>a</sup> Reference 37.<sup>b</sup> Reference 38.<sup>c</sup> Reference 39.<sup>d</sup> Reference 40.<sup>e</sup> Calculated from Eq. (9a) of Ref. 3.<sup>f</sup> Calculated from Eq. (9b) of Ref. 3.<sup>g</sup> Calculated from Eq. (9c) of Ref. 3.

not available and  $N_{\text{eff}}$  was approximated by taking the value of  $N_{\text{eff}}$  reported in the literature<sup>49</sup> for the isoelectronic system Ar also obtained from Eq. (8).

Next we estimate average excitation energies using the well-known formula for  $\Omega_1$  and new approximate expressions for  $\Omega_2$  and  $\Omega_3$  recently reported by Koutselos and Mason<sup>50</sup>:

$$\Omega_1 = (N/\alpha_1), \quad (9a)$$

$$\Omega_2 = \left( \frac{9N\alpha_1}{2\alpha_2} \right)^{1/4}, \quad (9b)$$

$$\Omega_3 = \left( \frac{15}{2} \right)^{1/2} \left( \frac{9N\alpha_2^2}{\alpha_3^4} \right)^{1/8}. \quad (9c)$$

In this way we have generated all the ingredients needed to apply the combining rules of Ref. 3 to the calculations of  $C_6$ ,  $C_8$  and  $C(1,3)$ . The results are listed in Table VI.

With these potential parameters we are in a position to finally calculate the dispersion constants for the  $\text{F}^-$  and  $\text{Cl}^-$  rare gas interactions using again the same combining rules of Ref. 3. The final results are tabulated in Table VII.

A comparison with another independent *ab initio* determination is only possible in the case of  $\text{F}^-$ -He and  $\text{Cl}^-$ -He interaction as indicated in Table VII. The agreement in both cases can be regarded as satisfactory. In particular, it leads to the support of our use of the McEachran *et al.* values for the dipole polarizabilities of  $\text{F}^-$  and  $\text{Cl}^-$ .

## V. RESULTS AND DISCUSSION

In view of the large differences in the expected precision in the input data as well as in our knowledge on the potentials of these systems from other sources we will organize the discussion by dealing with (1)  $\text{Li}^+$ -He, (2) the other positive ion-rare gas atom systems, and (3) the negative ion-rare gas systems, separately. Table VIII shows a summary of some recent experimental and theoretical determinations of the potential parameters  $R_0$ ,  $R_m$ , and  $\epsilon$  with the data sources for all the systems dealt with here. At the end of this section we will discuss a comparison, where possible, of systems within an isoelectronic group.

TABLE IV. Dispersion coefficients between positive ions and rare gases, all values are in a.u.

Coefficient:	$C_6$			$C_8$			$C_{10}$	
	a	b	other	a	b	other	a	b
$\text{Li}^+-\text{He}$	0.298	0.294	0.291 – 0.295 <sup>c</sup> 0.34 <sup>d,e</sup> 0.30 <sup>f</sup>	1.97	1.98	1.98 – 2.01 <sup>c</sup> 2.07 <sup>e</sup>	18.8	19.4
$\text{Li}^+-\text{Ne}$	0.679	0.67	...	4.65	6.15	...	46.3	78.0
$\text{Li}^+-\text{Ar}$	1.85	1.90	2.0 <sup>d</sup>	22.6	29.3	...	423	607
$\text{Na}^+-\text{He}$	1.43	1.41	1.346 – 1.423 <sup>g</sup>	13.6	13.5	12.10 – 12.79 <sup>g</sup>	162	163
$\text{Na}^+-\text{Ne}$	3.22	3.20	3.08 <sup>h</sup>	31.6	38.4	...	393	578
$\text{Na}^+-\text{Ar}$	9.04	9.32	...	137	170	...	2 840	3 882
$\text{K}^+-\text{He}$	5.83	5.79	7.1 <sup>d</sup>	80.7	80.0	...	1 350	1 356
$\text{K}^+-\text{Ne}$	12.6	12.7	...	184	209	...	3 170	4 152
$\text{K}^+-\text{Ar}$	39.0	39.9	47.2 <sup>d</sup>	770	893	...	18 800	24 370

<sup>a</sup> Present combining rule results calculated with input data in Tables I and II and with Eqs. (10a)–(10c) of Ref. 3 for  $C_6$ ,  $C_8$ ,  $C_{10}$ , respectively.

<sup>b</sup> Reference 39.

<sup>c</sup> Reference 35. The first value is from a coupled Hartree-Fock calculation and the second one is based on a semiempirical correction of the CHF value.

<sup>d</sup> Combining rule estimates reported by McDaniel and Mason, p. 253, Ref. 1.

<sup>e</sup> Reference 41.

<sup>f</sup> Reference 42.

<sup>g</sup> Reference 43.

<sup>h</sup> Reference 44.

TABLE V. Polarizabilities and effective number of electrons of  $F^-$  and  $Cl^-$ .

	$\alpha_1^a$	$\alpha_2^a$	$\alpha_3^a$	$N_{eff}$
$F^-$	10.66	76.7	1179	3.146 <sup>b</sup>
$Cl^-$	31.6	318	7384	5.870 <sup>c</sup>

<sup>a</sup> All polarizabilities have been taken from Ref. 45. More recent calculations suggest that the dipole polarizability may be too small by a factor of 2. See, for example, Ref. 44 and Ref. 45.

<sup>b</sup> Calculated from Eq. (8) with  $C_6$  taken from Ref. 44.

<sup>c</sup> Approximated by the value of  $N_{eff}$  for the isoelectronic system Ar.

### A. $Li^+$ and the rare gas atoms

Figure 4 shows the  $Li^+ - He$  potential and the various contributions to the final potential. For this system the dipole induction term alone accounts for 75% of the well minimum. Of the remaining 25%, about 75% are accounted for by the dipole polarizability. This suggests that by the inclusion of the hexadecapole polarizability and  $C_{10}$  term that the potential should be very nearly converged.

$Li^+ - He$  is the only system for which we can carry out a comparison with a previously published accurate *ab initio* calculation. The 1976 coupled electron pair approximation (CEPA) results of Hariharan and Staemmler<sup>13</sup> are still considered the most accurate *ab initio* calculation possible for any ion-atom van der Waals interaction. Figure 5 shows our predicted curve on the same plot as the CEPA calculation. The agreement over the entire range is excellent. The largest differences are found in the well region where the present potential is deeper at most by about 3%. It is interesting to note that the potential model used by Siska<sup>17</sup> which is very similar to that used in the present work agrees very well with both our predictions, and the CEPA calculations even though it uses fewer terms.

The good agreement of the model with the *ab initio* calculations seems to suggest that our method for taking into account the exchange induction and exchange dispersion terms, which together amount to 31% of the repulsive potential and a resulting increase in the well energy of about 25% is correct, at least for this one system.

Thus we can consider the predictions for  $Li^+$  interactions with the other rare gas to be also the most accurate among the systems dealt with. This is confirmed by the good agreement found between our potentials for  $Li^+ - Ne$ , Ar with previous calculations and experiments summarized in

TABLE VII. Estimated dispersion coefficients for the halide ion-rare gas atom interaction.<sup>a</sup>

	$C_6$	$C_8$	$C_{10}$
$F^- - He$	7.83(7.18) <sup>b</sup>	165	4450
$F^- - Ne$	16.3	358	9810
$F^- - Ar$	55.2	1530	52100
$Cl^- - He$	19.8(17.4) <sup>c</sup>	530	16760
$Cl^- - Ne$	40.7	1120	36050
$Cl^- - Ar$	142	4780	187000

<sup>a</sup> Calculated with input data in Tables II, V, and VI from the combining rules [Eqs. (10a)-(10c)] of Ref. 3 for  $C_6$ ,  $C_8$ , and  $C_{10}$ , respectively.

<sup>b</sup> Reference 35.

<sup>c</sup> Reference 43.

Table VIII. For  $Li^+ - Ne$  our potential agrees within the expected errors with the recent mobility potential determined by Viehland<sup>19</sup> and also with the electron gas potential of Waldman.<sup>51</sup> The other scattering experiments for  $Li^+ - Ne$  are not expected to be as reliable as the mobility determinations. In the case of  $Li^+ - Ar$  the well depth is in reasonable agreement with a direct determination from rainbow scattering and measurements of the energy dependence of integral cross sections. However, there appears to be a systematic disagreement with our predicted value of  $R_m$  which is smaller than all previously determined values, with the exception of the electron gas calculations of Waldman.

### B. The other positive ions and rare gas atoms

For the other alkali ion-rare gas atom interactions our predictions can not be considered as reliable because of the lack of accurate  $C_6$ ,  $C_8$ , and  $C_{10}$  dispersion coefficients. Figures 6 and 7 show the relative contributions of the various terms of the potential model to the final potential for  $Na^+ - Ar$  and  $K^+ - Ar$ . Because of the relatively large  $C_6$  dispersion constant, which is also large compared to the induced quadrupole moment induction term, the effect of the  $R^{-6}$  term is much larger, than in the case of  $Li^+ - He$ . Thus in  $K^+ - Ar$  the dipole induction term accounts for less than 50% of the potential at the minimum. This is characteristic for all of these systems and since the dispersion coefficients are much less certain than the polarizabilities the errors are expected to be larger.

The previous studies for the systems  $Na^+ - He$ ,  $Na^+ - Ne$  and  $K^+ - He$ , and  $K^+ - Ne$  probably allow a less critical com-

TABLE VI. Average excitation energies and dispersion coefficients of the negative ions.

	$\Omega_1^a$	$\Omega_2^b$	$\Omega_3^c$	$C_6$	$C_8$	$C(1,3)$
$F^- - F^-$	0.543	0.476	0.358	46.3 <sup>d</sup>	1550 <sup>f</sup>	18980 <sup>g</sup>
$Cl^- - Cl^-$	0.431	0.359	0.208	321.7 <sup>e</sup>	14730 <sup>f</sup>	227000 <sup>g</sup>

<sup>a</sup> Calculated from Eq. (9a).

<sup>b</sup> Calculated from Eq. (9b).

<sup>c</sup> Calculated from Eq. (9c).

<sup>d</sup> Reference 44.

<sup>e</sup> Calculated from Eq. (10a) of Ref. 3.

<sup>f</sup> Calculated from Eq. (10b) of Ref. 3.

<sup>g</sup> Calculated from Eq. (10d) of Ref. 3.

TABLE VIII. Comparison of potential parameters (in a.u.) from the present study with some previous experimental and theoretical studies. The values in parentheses are for dispersion coefficients up to  $C_8$  and induction coefficients up to  $\alpha_3$  only and provide an indication of the extent of convergence.

System	$R_0$	$R_m$	$\epsilon (\times 10^3)$	Source	Reference
$\text{Li}^+-\text{He}$	2.99(3.00)	3.57(3.58)	2.86(2.81)	present	
		3.60	2.56	electron gas	51
		3.70	2.34	SCF	11
	...	3.66	2.48	SCF	13
	...	3.63	2.74	CEPA(CI)	13
	...	3.70	2.73	mobilities	52
	$3.55 \pm 0.3$	$4.06 \pm 0.3$	...	scattering	54
	3.05	3.75	2.69	mobilities	19
	3.02	3.68	2.76	TTIA potential	17
$\text{Li}^+-\text{Ne}$	3.19(3.21)	3.77(3.80)	4.71(4.58)	present	
	...	3.70	4.5	electron gas	51
	$3.78 \pm 0.4$	$4.35 \pm 0.4$	...	scattering	54
	3.3	4.0	4.2	scattering	55
	3.3	3.9	4.5	mobilities	19
$\text{Li}^+-\text{Ar}$	3.59(3.63)	4.27(4.32)	12.3(11.7)	present	
	...	4.25	10.7	electron gas	51
	...	4.50	9.33	SCF	56
	...	4.50	9.97	CI	56
	$4.34 \pm 0.4$	$5.01 \pm 0.4$	...	scattering	54
	...	...	11.13	scattering	21
	3.80	4.60	10.0	mobilities	57
	3.70	4.55	11.7	scattering	55
$\text{Na}^+-\text{He}$	3.77(3.88)	4.41(4.44)	1.41(1.37)	present	
	3.95	4.5-5.0	1.00	SCF	12
	3.95	4.6	1.28	electron gas	51
$\text{Na}^+-\text{Ne}$	3.96(3.98)	4.57(4.60)	2.54(2.45)	present	
	3.80	4.59	2.79	electron gas	8
	3.95	4.6	2.42	electron gas	51
$\text{Na}^+-\text{Ar}$	4.42(4.45)	5.13(5.17)	6.59(6.31)	present	
	4.48	5.22	5.70	electron gas III	6
	...	5.20	5.95	electron gas	51
	...	6.50	4.37	scattering	58
	4.30	4.95	7.50	pseudo pot.	59
$\text{K}^+-\text{He}$	4.85(4.89)	5.50(5.61)	0.67(0.64)	present	
	...	$5.1 \pm 0.4$	$0.92 \pm 0.2$	mobilities	60
	4.4-4.29	4.74 - 5.01	0.81 - 0.96	scattering	22
	4.74	5.42	0.89	electron gas III	6
$\text{K}^+-\text{Ne}$	4.93(4.98)	5.62(5.68)	1.33(1.25)	present	
	4.42 - 4.52	5.06 - 5.23	1.43	scattering	22
	4.78	5.44	1.65	electron gas III	6
	...	...	1.45	electron gas	51
	4.95	5.6	1.58	mobility	61
	4.67	5.29	2.27	mobility	62
	...	5.39	1.48	model pot.	18
$\text{K}^+-\text{Ar}$	5.40(5.45)	6.19(6.25)	3.48(3.30)	present	
	4.8	5.5	4.48	electron gas	8
	5.1	5.9	4.06	electron gas	51
	5:50	6.28	3.12	mobility	63
	5.0	5.7	4.5	mobility	64
	4.5	5.4	5.0	mobility	65
	4.74 - 4.86	5.29 - 5.67	4.3 - 5.18	scattering	22
	...	6.59	3.45	scattering	58
	4.95	5.65	4.55	model pot.	59
	...	5.79	4.20	model pot.	18
$\text{F}^--\text{He}$	4.70(4.81)	5.47(5.59)	0.79(0.65)	present	
	4.80	5.65	0.65	electron gas III	6
	5.4	6.4	0.24	SCF	47
	5.4	6.5	0.29	4th order many body perturbation theory	47
	4.65	...	...	mobilities	66



TABLE VIII (continued).

System	$R_0$	$R_m$	$\epsilon (\times 10^3)$	Source	Reference
$F^- - Ne$	5.07(5.16)	5.92(6.00)	0.99(0.90)	present	6
	5.18	6.05	0.89	electron gas III	
$F^- - Ar$	4.80(4.91)	5.67(5.80)	4.70(4.14)	present	6
	4.74	5.69	4.19	electron gas III	
	4.554	5.255	5.03	mobilities	
$Cl^- - He$	6.73(6.82)	7.75(7.84)	0.20(0.18)	present	6
	5.84	6.77	0.44	electron gas III	
	5.332	...	...	mobilities	
$Cl^- - Ne$	6.42(6.52)	7.41(7.52)	0.48(0.43)	present	6
	6.35	7.31	0.52	electron gas III	
	5.679	...	...	mobilities	
$Cl^- - Ar$	6.10(6.23)	7.08(7.24)	2.36(2.06)	present	6
	5.56	6.60	2.90	electron gas III	
	5.33	5.938	3.81	mobilities	
	6.8	8.0	0.87	SCF	

parison than for the more extensively studied systems  $Na^+ - Ar$  and  $K^+ - Ar$ . Thus we will concentrate in the following discussion on these two systems.

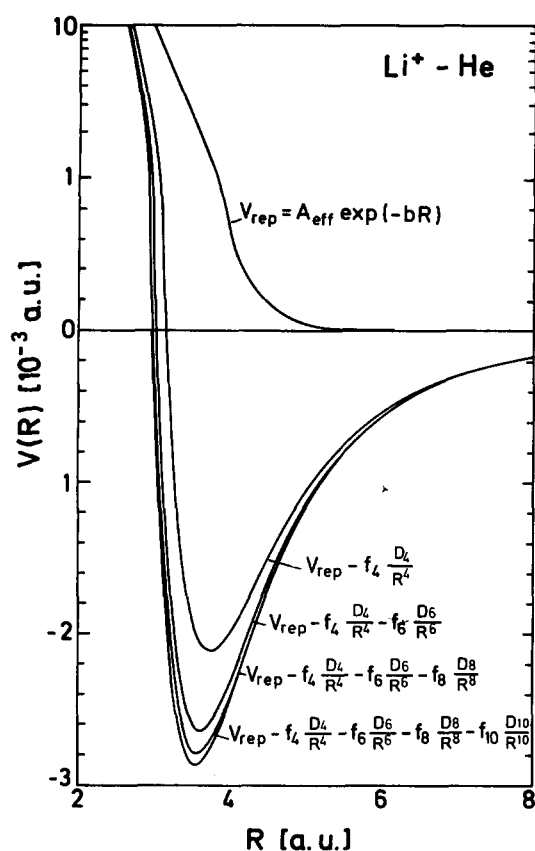


FIG. 4. The relative contributions of the different terms in the total potential are shown for the  $Li^+ - He$  system. The uppermost repulsive curve shows only the effective Born-Mayer repulsive potential. The bottom three curves show the effect of adding successively the different attractive terms to the potential. The bottommost curve is the final potential predicted by the model.

The best previous data for  $Na^+ - Ar$  come from a different pseudopotential calculation<sup>61</sup> and a recent electron gas calculation.<sup>51</sup> If we take the average of these three determinations we obtain the following values,  $R_m = 5.05$  and  $\epsilon = 6.65 \times 10^{-3}$  in very good agreement with our values of  $5.15$  and  $6.51 \times 10^{-3}$ , respectively. The very early scattering

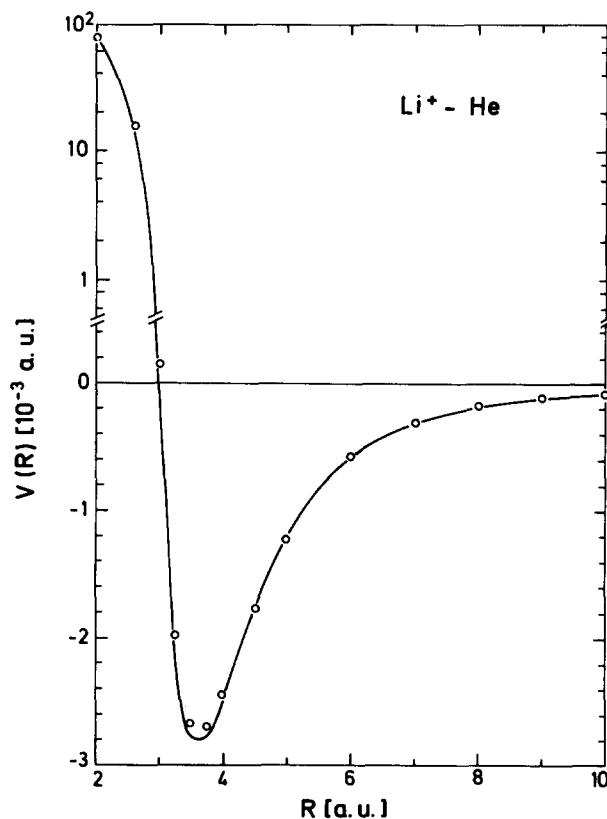


FIG. 5. Comparison of the present potential for  $Li^+ - He$  (—) with the *ab initio* CEPA calculated points (○) of Hariharan and Staemmler (Ref. 13). The agreement is everywhere better than 3%.

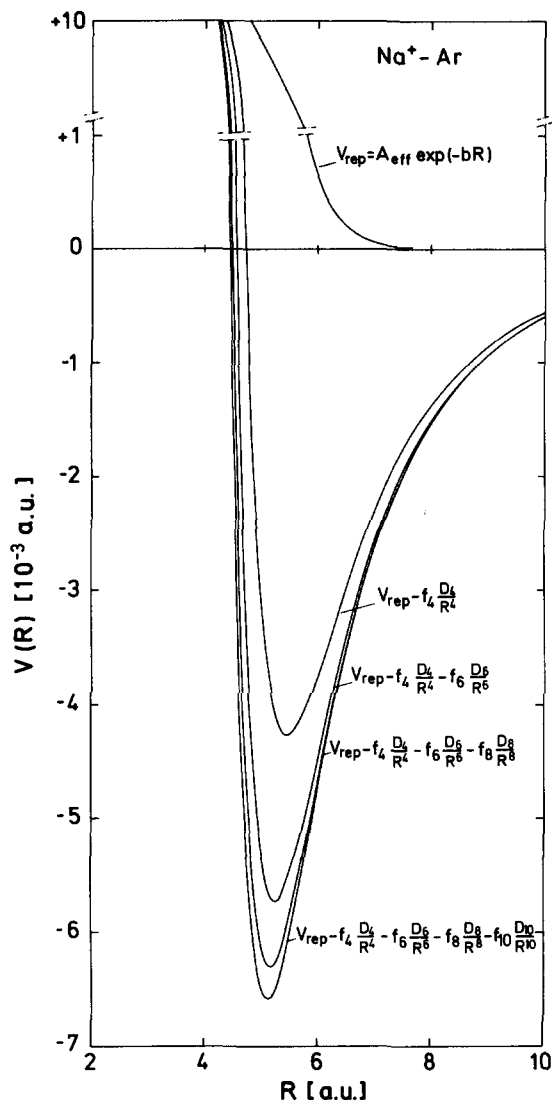


FIG. 6. The relative contributions of the different terms in the total potential are shown for the  $\text{Na}^+ - \text{Ar}$  system. The uppermost repulsive curve shows only the effective Born-Mayer repulsive potential. The bottom three curves show the effect of adding successively the different attractive terms to the potential. The bottommost curve is the final potential predicted by the model.

experiments of Powers and Cross<sup>58</sup> are probably not very accurate. Other experiments are not known to us.

SCF, configuration interaction (singles and doubles) [CI(SD)], and coupled pair function (CPF) calculations have been performed for  $\text{Na}^+ - \text{Ar}$  in order to provide an even more accurate check of the results of the present method. The recently proposed CPF method is a size consistent modification of the CI(SD) technique based on an energy functional formulation,<sup>67</sup> it is closely related to CEPA(1) procedures.<sup>68</sup> Since the CPF energy accounts for effects of higher (than double) substitutions it is considered to be more reliable than the CI(SD) energy and we will mainly rely on the CPF results.

The following basis sets have been used:

Ar:  $(12 + 1s, 9 + 1p, 3d, 2f)/[8, 6, 3, 2]$   
 $\eta_d = 2.6, 0.76, 0.22; \eta_f = 1.5, 0.4,$   
 diffuse functions:  $\eta_s = 0.09, \eta_p = 0.06,$

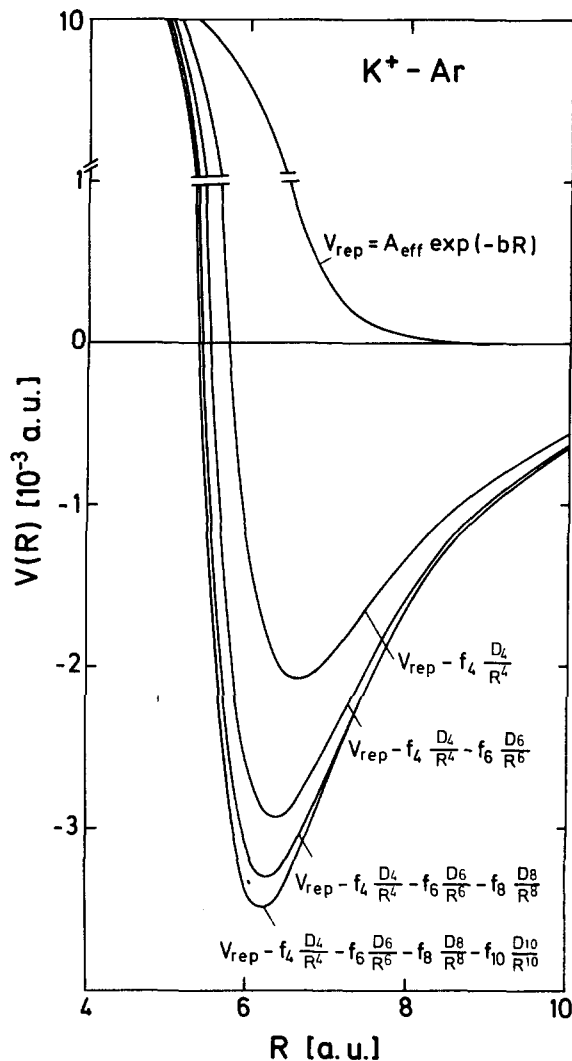


FIG. 7. The relative contributions of the different terms in the total potential are shown for the  $\text{K}^+ - \text{Ar}$  system. The curves correspond to the same contributions as shown in Fig. 4 for  $\text{Li}^+ - \text{He}$ . In comparing the two systems we see that for  $\text{K}^+ - \text{Ar}$  the  $C_6$  dispersion term makes a relatively larger contribution than in  $\text{Li}^+ - \text{He}$ .

$\text{Na}^+$ :  $(11s, 7p, 3d, 2f)/[7, 4, 3, 2],$   
 $\eta_d = 2.7, 0.85, 0.3; \eta_f = 1.6, 0.5.$

The primitive Gaussians, (12,9) for argon and (11,7) for  $\text{Na}^+$ , were again taken from Huzinaga's tables.<sup>34</sup> In order to get an indication of the basis set superposition errors we have evaluated counterpoise corrections<sup>33</sup> for a few values of  $R$ .

The results of the calculations are collected in Table IX. It is difficult to assess the reliability of the results since interatomic interactions for such large systems are very difficult to compute. However, the basis set should be sufficiently flexible to yield SCF level interaction energies with an accuracy of a few percent. This is supported by the smallness of the counterpoise correction which amounts to only 2% of the SCF interaction energy, at the calculated value of the well location  $R = 5.3$  a.u.

TABLE IX.  $\text{Na}^+ - \text{Ar}$  interaction energies as obtained on various levels of approximation. The energies are in mhartree. The results in parentheses denote the corresponding counterpoise corrections as explained in the text. The CPF well parameters are  $R_m = 5.24$ ,  $\epsilon = -5.97$ .

$R$	SCF	CI(SD)	CPF
14.0	-0.131	-0.135	-0.137
12.0	-0.250	-0.258	-0.262
11.0	-0.360	-0.375	-0.381
10.0	-0.542	-0.570	-0.579
9.0	-0.855	-0.908	-0.924
8.0	-1.416	-1.519	-1.550
	(-0.022)	(-0.060)	(-0.062)
7.0	-2.437	-2.649	-2.708
6.0	-4.075	-4.578	-4.691
5.5	-4.766	-5.590	-5.740
5.3	-4.780	-5.791	-5.957
	(-0.076)	(-0.365)	(-0.379)
5.0	-4.088	-0.467	-5.655
4.5	1.588	-0.732	-0.960
4.0	22.517	18.605	18.318
	(-0.142)	(-1.303)	(-1.370)

The intra- and interatomic contributions to the correlation energies converge much slower on basis set extension than SCF energies. This is demonstrated by the counterpoise correction (at  $R = 5.3$  a.u.) of 0.000 379 a.u. to the CPF energy which, although relatively small in comparison with the total correlation energy, amounts to 32% of the CPF correlation energy contribution to  $\epsilon$  ( $-0.001\,177$  a.u.). The correlation energy contribution  $\epsilon_c$  to  $\epsilon$  should, therefore, be somewhere in between  $-0.001\,18$  and  $-0.000\,80$  a.u. for the present basis set. Since additional basis functions will still contribute considerably ( $\sim 35\%$ ) to the interatomic dispersion-type contributions we estimate (for  $R_m \approx 5.3$  a.u.)

$$-0.0016 \text{ a.u.} \leq \epsilon_c \leq -0.0010 \text{ a.u.}$$

This leads to a total well depth of

$$\epsilon = -0.0063 \pm 0.0003 \text{ a.u.},$$

which is to be compared with the value from the present model  $\epsilon = -0.0065$  a.u. (Table IX). The overall agreement of the *ab initio* and model potential curve is shown in Fig. 8 and is well within the errors of both evaluations and provides additional confirmation for the validity of the present model for a “heavy” system.

$\text{K}^+ - \text{Ar}$  has probably been studied experimentally more than any other of the ion-atom systems. Nevertheless, the uncertainty in the potential must still be considered to be rather large. The most recent experimental study is that of Budenholzer *et al.*<sup>22</sup> They have considered several model potentials in the search for a best fit of their integral cross section measurements. Three potentials were found to give nearly equivalent fits and the values bracketted by these potentials are given in the  $\text{K}^+ - \text{Ar}$  entry in Table VIII. These values do not overlap with the results of our calculations and our predicted  $R_0$  and  $R_m$  values are larger and our well depth  $\epsilon$  is smaller than most of the other determinations with the exception of the only SCF calculations of Ref. 63. Also there is quite large disagreement with the results of Ref. 18 based on a similar model. This apparent disagreement has led us to reexamine the input data for this system. As seen in

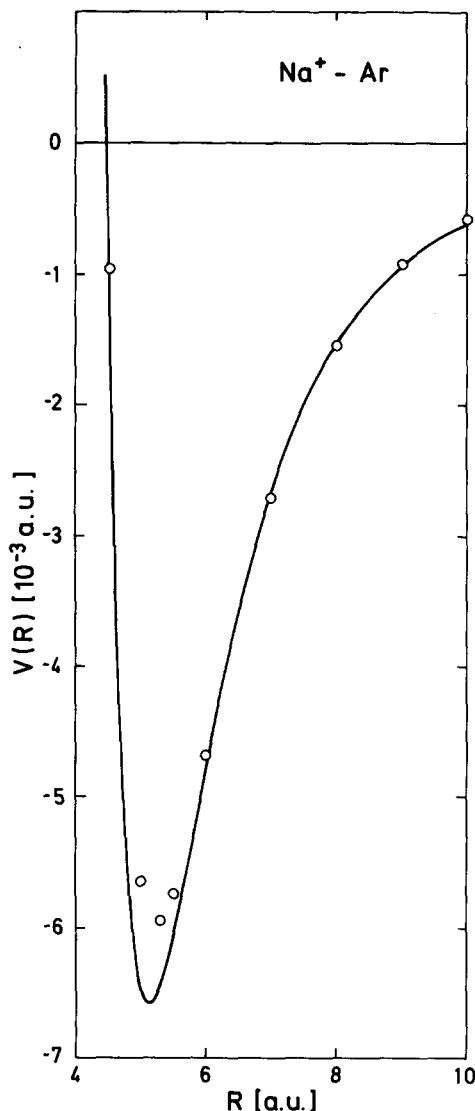


FIG. 8. Comparison of the present model potential (—) for  $\text{Na}^+ - \text{Ar}$  with the *ab initio* CPF calculated points (○) also of the present paper.

Fig. 3 it appears as if the Born-Mayer parameters for  $\text{K}^+ - \text{Ar}$  do not follow the same trend with respect to the other isoelectronic systems as found for the analogous set of systems shown in Fig. 2. For this reason the  $\text{K}^+ - \text{Ar}$  Born-Mayer parameters were recalculated with a larger basis set and the values of  $A$  and  $b$  were found to change only insignificantly. Thus at the present time we cannot explain the apparent discrepancy for this system within the framework of our model.

It is worth mentioning that if we use older experimental values of  $A = 327$  and  $b = 2.0948$ <sup>69</sup> which are in agreement with an early calculation by Sida<sup>70</sup> we obtain  $R_0 = 4.86$ ,  $R_m = 5.62$ , and  $\epsilon = 5.02 \times 10^{-3}$  in much better agreement with other work in Table VIII. In view of the new calculations reported here we can no longer accept these older values of  $A$  and  $b$ . But this observation may suggest that in the case of  $\text{K}^+ - \text{Ar}$  the factor 1.31 introduced into the model to account for  $E_{\text{ex disp}}$  and  $E_{\text{ex ind}}$  [see Eqs. (3) and (4)] is too large. Note that  $\text{K}^+ - \text{Ar}$  has the largest number of electrons of all

systems investigated here. Thus it is conceivable that for large systems the factor 1.31 has to be reduced. Future theoretical and experimental results will eventually help us to establish how this correction factor varies from system to system.

### C. The negative ions and rare gas atoms

In the case of the negative ions and the rare gas atoms we do not anticipate nearly as high an accuracy of our predictions. We nevertheless present them here because of the large uncertainties of other determinations. Figure 9 reveals that with regard to the relative contribution from the dispersion forces the situation in  $F^-$ -He is quite similar to  $K^+$ -Ar. In  $F^-$ -He the major contribution to the dispersion force comes from the very polarizable  $F^-$ -ion, since the He atom has a very small static and dynamic polarizability. As indicated in Table VIII there is a very substantial disagreement between our prediction of  $\epsilon$  and  $R_m$  and the latest *ab initio* calculations of Diercksen and Sadlej.<sup>47</sup> In their extensive study these authors also present results from a third order many-body perturbation calculation, which predicts  $\epsilon = 0.453 \times 10^{-3}$  a.u. which is deeper but still off by almost a factor of 2 from our value. In their calculation they found that the second order dispersion energy is almost completely damped out at the well minimum and indeed if we were to neglect the dispersion term altogether we would come much closer to their values for both  $\epsilon$  and  $R_m$ . On the other hand, there is some indication that their results are not well con-

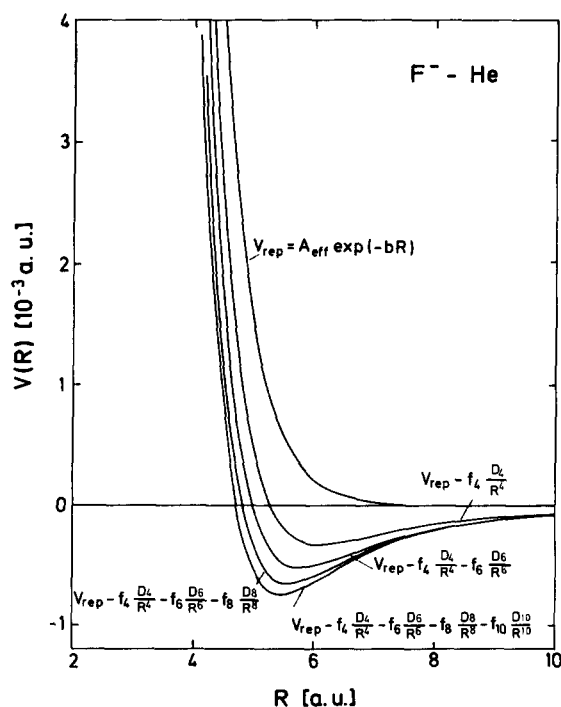


FIG. 9. The relative contributions of the different terms in the total potential are shown for the  $F^-$ -He system. The curves correspond to the same contributions as shown in Fig. 4 for  $Li^+$ -He and in Fig. 6 for  $K^+$ -Ar. In  $F^-$ -He the relative contribution from the  $C_6$  dispersion term is even larger than for the other system.

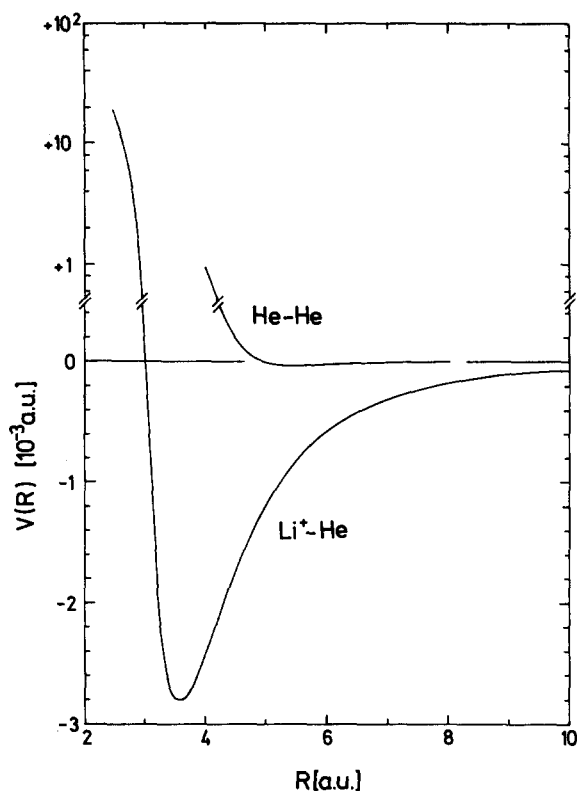


FIG. 10. Comparison of van der Waals potential curves of the isoelectronic He-He and  $Li^+$ -He systems.

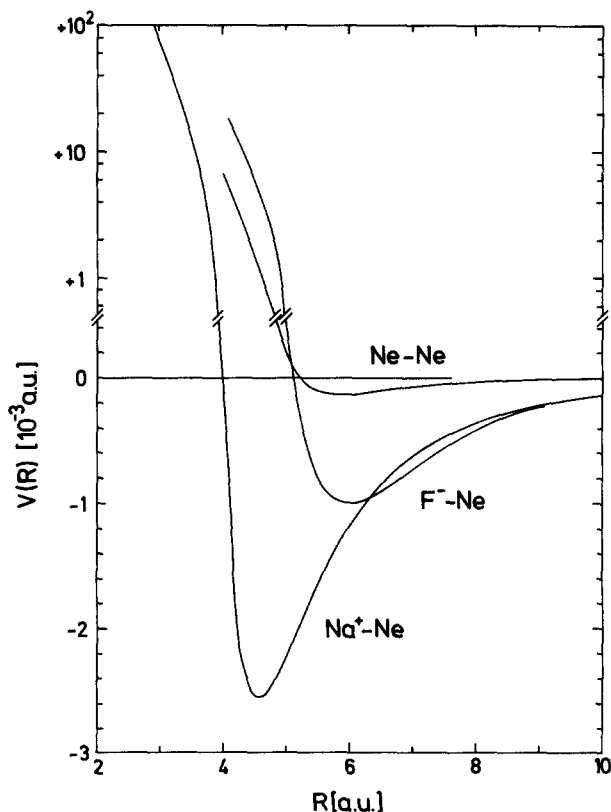


FIG. 11. Comparison of the van der Waals potential curves of the isoelectronic Ne-Ne,  $Na^+$ -Ne, and  $F^-$ -Ne system. Note that for Ne-Ne and  $F^-$ -Ne the well locations are nearly the same even though the well depths are vastly different.

verged since the third order and fourth order terms in their calculations nearly cancel each other. The recent analysis of Kirkpatrick and Viehland<sup>66</sup> of experimental mobilities yields a value of  $R_0$  which agrees very well with our prediction. Unfortunately they could not determine  $\epsilon$ . They have estimated the errors in their potentials to be of the order 20%–25%.

In the case of the other negative ions the agreement with the early electron gas model calculations<sup>6</sup> is fairly good. For  $F^-$ -Ar we get surprisingly good agreement with the potential of Kirkpatrick and Viehland.<sup>66</sup> For  $Cl^-$ -He,  $Cl^-$ -Ne, and  $Cl^-$ -Ar, on the other hand, we find rather large discrepancies with regard to  $R_0$ . For  $Cl^-$ -Ar our potential will come closer to the mobility data if either our  $C_6$  were too small or the repulsive potential too repulsive.

#### D. Comparison of isoelectronic series

Finally in Figs. 10–12 we compare the potential curves for the three sets of isoelectronic systems which have become

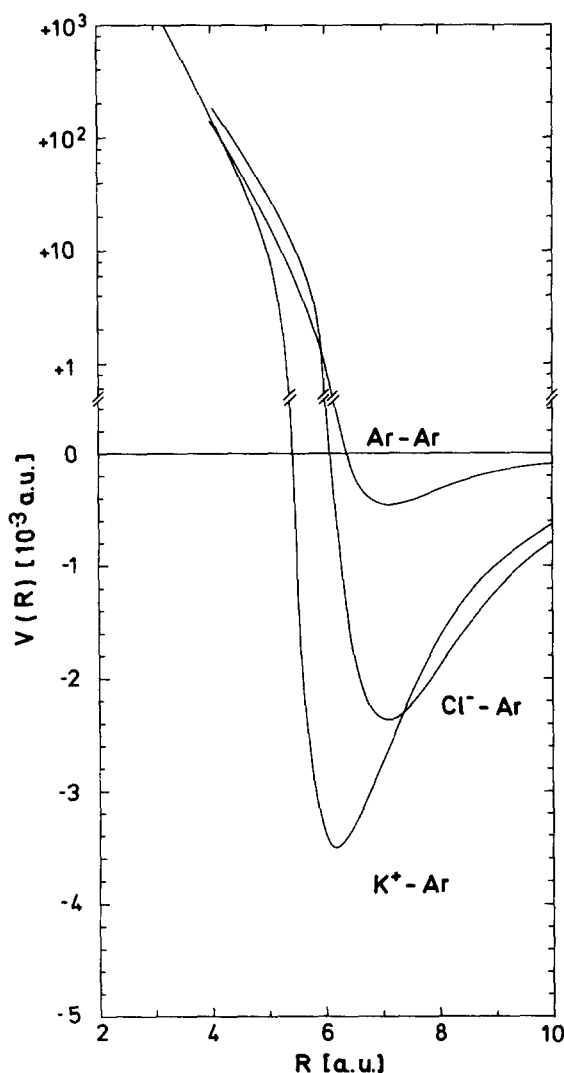


FIG. 12. Comparison of the van der Waals potential curves of the isoelectronic Ar-Ar,  $K^+$ -Ar, and  $Cl^-$ -Ar systems. Note that for Ar-Ar and  $Cl^-$ -Ar the well locations are nearly the same even though the well depths are vastly different.

available as a result of this study. Some interesting trends are worth noting. Of course the ion-atom potentials are much deeper as expected from the inductive potential. In Figs. 11 and 12 it is perhaps surprising to see that the well depths of negative ion potentials are about 50%–65% smaller than for the positive ions. The presence of the diffuse orbitals in the negative ions provides both a longer range repulsion and a longer range attraction. This tends to shift the potential minimum further out and weakens the bond. Also it is surprising to find that the well locations for the neutral partners is about the same as for the corresponding negative ion-atom interactions.

To the extent that our potentials are correct this suggests that in going from an atom-atom to a negative ion-atom interaction that the relative increase in the repulsive and attractive potentials has a fixed definite relationship.

#### ACKNOWLEDGMENTS

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