

Atomic Distortion and the Combining Rule for Repulsive Potentials

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The exponential repulsion between atoms, molecules, and ions with closed-shell structure arising from the Pauli exclusion principle is examined in the light of a distortion model. The repulsion energy arises mainly from the distortion of the two atoms, each of which is constrained by the presence of the other to terminate at an intermediate surface, which is often approximately planar. The location of this surface is determined by minimizing the total distortion energy, with the result that the restoring forces in each atom are equal and opposite. There results a new combining rule for these repulsive potentials, allowing the potential for AB to be deduced from those for A_2 and B_2 , which reduces in some special cases to the previously assumed geometric-mean rule. A further consequence is a relationship between the instantaneous collisional dipole moments in a family of asymmetric collisions such as HeNe, NeAr, and ArHe, provided that they are all measured at equal values of the collision force.

The repulsive interaction maintaining the integrity and separation of atoms, molecules, and ions with a closed-shell structure has long been known to have a remarkably simple character. It is usually very well represented by a simple exponential function over two or more decades in the potential energy, typically covering the range between 0.1 and 10 eV or beyond. The physical source of this repulsion is primarily the Pauli exclusion principle, which effectively prevents the overlapping of the electron clouds of the outer shells of the colliding partners. The exponential form arises from the exponential tail in the electron density distribution about each atom or molecule. This repulsive interaction dominates small-angle atomic and molecular scattering even into the keV region, and it has a major role in determining the interionic or interatomic spacing in the ionic solids as well as in atomic or molecular liquids and gases. Considerable effort has gone into the empirical search for a combining rule allowing the repulsive potential for a mixed system such as AB to be deduced from the potentials for two known systems AA and BB .¹⁻³

Most commonly, the combining rule is assumed to have the form of a geometric mean of the symmetric potentials:

$$[V_{12}(r)]^2 = V_{11}(r)V_{22}(r). \quad (1)$$

A typical example, shown in Fig. 1, appears to give empirical confirmation of this rule, but good theoretical justification is notably lacking. Indeed, it is somewhat surprising to find potentials for large and small atoms being compared at equal values of r , where the intensity of the disruptive forces acting on the outer electron shells at a fixed distance such as $1a_0$ or $2a_0$ must be extremely different as we pass through a sequence such as the rare gases from He to Xe or Rn.

The apparent success of the geometric-mean

rule is probably an accident arising from a combination of two circumstances, namely, that the repulsive potentials are essentially exponential in form, and that the range of the exponential decay happens to be almost constant in the families in which the rule has been most carefully tested. As Fig 2 illustrates, the range (the reciprocal of the logarithmic slope) is sometimes subject to fairly large variations.

The exponential potential can be written in several equivalent forms:

$$V_{ij} = A_{ij} e^{-r/\rho_{ij}} \quad (2)$$

$$= E_0 e^{(y_{ij}-r)/\rho_{ij}} \quad (3)$$

$$= F_0 \rho_{ij} e^{(x_{ij}-r)/\rho_{ij}}, \quad (4)$$

where E_0 is a standard energy, F_0 is a standard force, ρ is the range of the potential, and y and x are lengths characterizing the particular colliding pair. Obviously, the transition from curve to curve in Fig. 1 could be described equally well by a horizontal shift representing successive increases

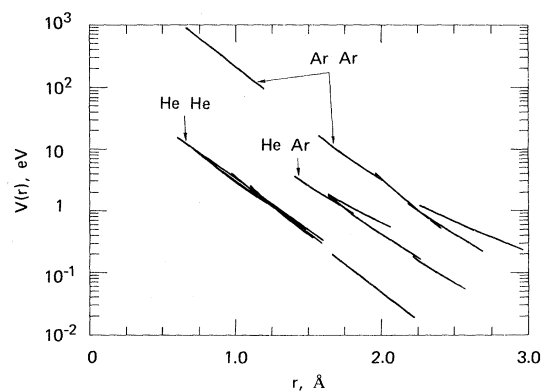


FIG. 1. Measured potentials for He₂, HeAr, and Ar₂: He₂ from Refs. 4-8; HeAr from Refs. 7 and 9-11; Ar₂ from Refs. 7, 9, and 12-14.

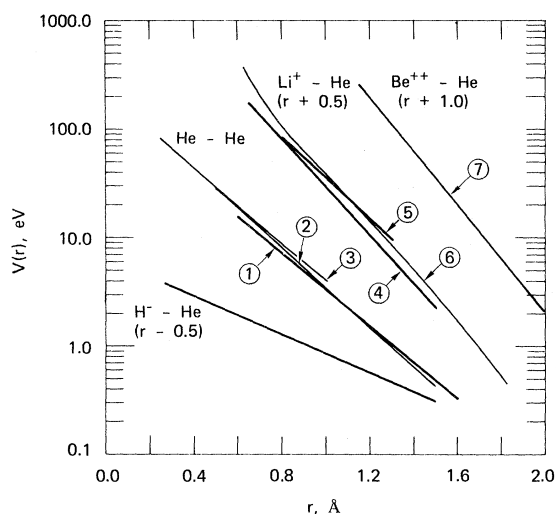


FIG. 2. Potentials for He with H^+ , He, Li^+ , and Be^{++} . H^+He : Ref. 15. He_2 : curve 1, combined experiments, Refs. 4-8; curve 2, Ref. 16; curve 3, Ref. 17. Li^+He : curve 4, Ref. 18; curve 5, Ref. 19; curve 6, Refs. 20-22. $Be^{++}He$: curve 7, Ref. 23.

in size as one goes from He_2 to $HeAr$ and then to Ar_2 , instead of the vertical shift that would be implied by the geometric-mean rule. When the ρ 's are essentially equal, the combining rule could be described by either

$$y_{ij} = \frac{1}{2}(y_{ii} + y_{jj}) \quad (5)$$

or

$$x_{ij} = \frac{1}{2}(x_{ii} + x_{jj}) \quad (6)$$

What happens when the ρ 's are not identical? This question can be answered by a closer examination of the effect of the exclusion principle that creates the exponential repulsion. As Matcha and Nesbet²⁴ have remarked, the exclusion principle causes the electron clouds in each of a pair of colliding atoms to be distorted and flattened as if there were an impenetrable barrier surface between the two atoms. In symmetric (AA) collisions, the surface is obviously a plane equidistant from both nuclei; in asymmetric cases (AB), the surface may often be approximated by a plane lying at some unknown distance r_A between the two nuclei. It is plausible to assume that the repulsive energy is simply the sum of the distortion energies internal to the two atoms A and B and therefore dependent only on the distances r_A and $r_B = r - r_A$:

$$V_{AB}(r; r_A) = \frac{1}{2}V_{AA}(2r_A) + \frac{1}{2}V_{BB}[2(r - r_A)] \quad (7)$$

Clearly, the distortion plane will settle at such a distance r_A as to minimize the total energy; the result is that the restoring forces in the two atoms are equal and opposite:

$$\left(\frac{dV_{AA}(r)}{dr}\right)_{r=2r_A} = \left(\frac{dV_{BB}(r)}{dr}\right)_{r=2r_B} \quad (8)$$

Equations (7) and (8) give a prescription for combining any repulsive potentials in the region where they arise predominantly from the effect of the exclusion principle.

If the potentials for the symmetric systems are exponential in form, application of Eqs. (7) and (8) shows that the potential for the asymmetric case is also a simple exponential with a range ρ_{ij} , that is, exactly the arithmetic mean of the symmetric ρ 's:

$$\rho_{ij} = \frac{1}{2}(\rho_{ii} + \rho_{jj}) \quad (9)$$

The appropriate form for the potential is that of Eq. (4), and the atomic sizes x combine exactly by Eq. (6). Unlike the range ρ , the size x depends on the choice of a standard force F_0 :

$$x_{ij} = \rho_{ij} \ln(A_{ij}/\rho_{ij}F_0) \quad (10)$$

However, if the potential is expressed in the form of Eq. (2), it is seen that the combining rule does not really depend on F_0 ; instead it is expressed by Eqs. (9) and (11):

$$(A_{ij}/\rho_{ij})^{2\rho_{ij}} = (A_{ii}/\rho_{ii})^{\rho_{ii}} (A_{jj}/\rho_{jj})^{\rho_{jj}} \quad (11)$$

In comparing interactions in different colliding systems at the same value of the restoring force, it is sometimes useful to introduce a reduced variable common to all the systems:

$$q = (r - x_{ij})/\rho_{ij} \quad (12)$$

This variable is a direct measure of the repulsive force:

$$F_{ij}(r)/F_0 = e^{-q} \quad (13)$$

Equations (4), (6), and (9) [or Eqs. (4), (9), and (11)] give the combining rule in the distortion model. If the ranges ρ happen to be the same, the result is identical with the geometric-mean rule, but it deviates significantly from that rule if they are not the same.

This combining rule can be used in several ways to predict potentials for various systems from a knowledge of those for others. A particularly stringent test is shown in Fig. 3 and Table I, where Matcha and Nesbet's calculated potentials²⁴ for the three systems $HeNe$, $HeAr$, and $NeAr$ are used to extract the potentials for He_2 , Ne_2 , and Ar_2 . The superiority of the distortion combining law over the geometric-mean law is clear, and the symmetric potentials extracted are in most gratifying agreement with the best existing direct calculations. In the cases of He_2 and Ne_2 , they are also in very satisfactory agreement with the experiments, but all the molecular-orbital calculations for Ar_2 are still significantly higher than the experimental po-

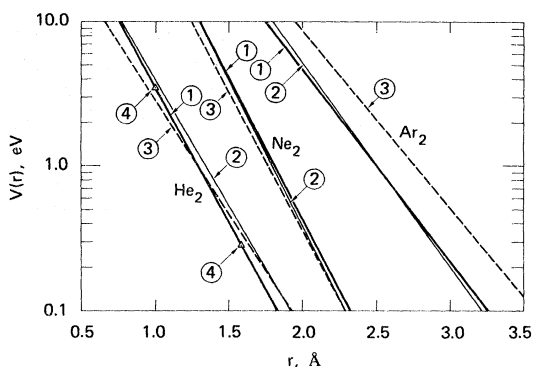


FIG. 3. Test of combining rules. Potentials for He_2 , Ne_2 , and Ar_2 deduced from data of Ref. 24 for HeNe , HeAr , and NeAr : 1, curves deduced by distortion rule; 3, curves deduced by geometric mean. Direct calculation: 2, curves of Ref. 25; 4, points from Ref. 17.

tentials.

In the case of the neutral rare gases, the ranges ρ vary only slightly from each other. As a result, to prove experimentally that the distortion combining rule is superior to the geometric-mean rule would require data of unattained accuracy and consistency. Current experiments are consistent with either rule. The discrepancies between experiment and the best molecular-orbital calculations^{24,25} for the systems containing Ar are all consistent with each other: For both HeAr and NeAr the experimental potentials fall below the calculations by a factor of about 0.6, and for Ar_2 the discrepancy is a factor of roughly 0.4; in all cases the experimental logarithmic slopes are somewhat greater than the molecular-orbital predictions (see Ref. 27 for a presentation of the data).

The combining rule arising from the distortion model can be used to make new and interesting connections between repulsive potentials for atom-atom, ion-atom, and ion-ion systems. For example, using information currently available for the pure rare gas systems and for the ion-atom collisions of K^+ and Cl^- with He, Ne, and Ar, one can estimate the short-range repulsive parameters for the systems $(\text{K}^+)_2$ and $(\text{Cl}^-)_2$, and thence the short-range repulsion term in KCl , for comparison with information obtained directly from the alkali halide molecules and solids. These and other applications to the alkali halides are being reported elsewhere.²⁷ Gilbert²⁸ has treated the alkali halides in an analogous manner, and suggested on empirical grounds the combining rules for ρ and x that I have derived here from the distortion model.

In addition to the potentials, Matcha and Nesbet²⁴ concerned themselves with the electrostatic dipole moment induced in each atom by the distortion of the electron cloud and with the resultant transient dipole moment of the diatomic system. If the dis-

tortion model is correct, dipole moments should be compared at equal values of the restoring force, that is, at equal values of q . Furthermore, since the resultant dipole moment is the difference between two atomic moments,

$$\mu_{AB}(q) = \mu_A(r_A(q)) - \mu_B(r_B(q)), \quad (14)$$

we expect a cyclic relation to hold,

$$\mu_{AB}(q) + \mu_{BC}(q) + \mu_{CA}(q) = 0. \quad (15)$$

Departures from Eq. (15) would reflect a deviation from the assumptions of the distortion model, especially that of planarity of the distortion surface between the colliding atoms. Indeed, one might expect the combining rule for potentials to be much better obeyed than the combining rule for dipole moments, because the dipole moment represents higher-order corrections than the potential; even an overlap between two unperturbed atoms without dipole moments will provide a reasonable estimate of the potential. Thus, Eq. (15) is a more stringent test of the distortion model than the combining rule for the potentials themselves.

Matcha and Nesbet's results showed that the diatomic dipole moments could be represented moderately well by simple exponentials. Using q as the variable in the form

$$\mu_{ij} = N_{ij} e^{-\gamma_{ij} q}, \quad (16)$$

we find $\gamma = 1.032$, 0.781 , and 0.795 for HeNe , HeAr , and NeAr , respectively, i.e., γ is always close to 1. It is thus convenient to remove the principal exponential dependence by writing

$$M_{ij}(q) = \mu_{ij} e^q \quad (17)$$

and to examine the quantities $M_{ij}(q)$ for their obedience to the cyclic relation of Eq. (15). Matcha

TABLE I. Collision parameters for systems containing He, Ne, and Ar.

	A (a. u.)	$\rho(a_0)$	$x(a_0)^a$
HeNe^b	33.418	0.4307	1.8740
HeAr^b	31.395	0.5308	2.1656
NeAr^b	92.544	0.5200	2.6945
He_2^c	9.2954	0.4414	1.3451
Ne_2^c	128.370	0.4199	2.4029
Ar_2^c	76.508	0.6201	2.9861
He_2^d	8.6997	0.4466	1.3262
Ne_2^e	150.430	0.4085	2.4137
Ar_2^e	129.110	0.5814	3.1413

^aAssuming $F_0 = 1$ a. u.

^bData from Ref. 24.

^cCalculated from data of Ref. 24, using Eqs. (6), (9), and (11).

^dReference 25.

^eReference 26.

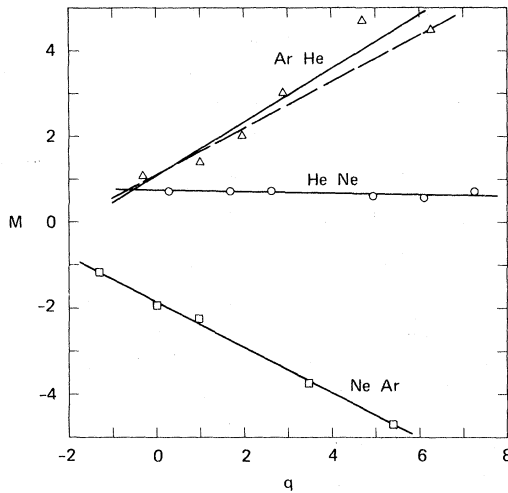


FIG. 4. Relation between dipole moments as a function of distortion force F . $q = \ln(F/F_0)$, $F_0 = 1/a_0$ a.u., $M_{ij} = \mu_{ij} e^a$. Solid lines are least-squares fits; dashed line represents $M_{ArHe} = M_{HeNe} - M_{NeAr}$. Data are from Ref. 24.

and Nesbet's data for HeNe, NeAr, and ArHe are plotted in this form in Fig. 4. The data for HeNe and NeAr are quite linear over the range of q covered by the calculations, and the ArHe results are either noisy or nonlinear. Least-squares fits, with error limits quoted as σ , the standard error, give the following linear equations:

$$\begin{aligned} M_{HeNe} &= (0.740 \pm 0.010) - (0.014 \pm 0.046)q, \\ M_{NeAr} &= -(1.863 \pm 0.017) - (0.521 \pm 0.049)q, \\ M_{ArHe} &= (1.093 \pm 0.105) + (0.621 \pm 0.363)q, \\ \sum M_{ij} &= -(0.030 \pm 0.107) + (0.086 \pm 0.369)q. \end{aligned} \quad (18)$$

Within the apparent scatter of the data, the relation (15) is seen to be obeyed.

This satisfactory empirical confirmation of Eq. (15) makes it worthwhile to seek an estimate of the individual atomic dipole moments as a function of the distortion force F (i.e., the parameter q). In the future, I hope that this dipole moment (and perhaps higher moments) will be reported with calculations of interatomic repulsive potentials, at least for symmetric diatomic pairs. In the meantime, the fragmentary reported data can be used for rough estimates. In particular, from very early calculations on He₂ and Ne₂, Matcha and Nesbet²⁴ report the estimated atomic dipole moments shown in Table II, from which values of M can be deduced. Unfortunately, these values are given only for a single internuclear distance r in each case, whereas we would like to know the dependence of the atomic moments on r or q . However, by using Eq. (14) it is possible to deduce a

second value for M_{He} and M_{Ne} , although this requires combining data from a later and more accurate calculation for the asymmetric system HeNe with results of earlier and less accurate²⁹ calculations for He₂ and Ne₂.

Taking the results in Table II at face value, it might appear that M_{He} and M_{Ne} have a very steep dependence on q . If the M 's are assumed to depend linearly on q , we would have $M_{He} = 0$ at $q = 6.12$ and $M_{Ne} = 0$ at $q = 8.55$, but there appears to be no reason to expect such a reversal of the dipole moments, given the nature of the wave functions employed in the calculations. It is much more likely that the disparity between the two values for M_{He} or M_{Ne} in Table II reflects uncertainties in the calculations rather than a true dependence on q . Therefore, it seems best at present to use the mean values

$$\bar{M}_{He} \cong 2.7D, \quad \bar{M}_{Ne} \cong 2.0D. \quad (19a)$$

Fortunately, the data of Fig. 4 are consistent with the possibility that M_{He} and M_{Ne} are independent of q , and with that assumption we find

$$M_{Ar} \cong 3.9 + 0.52q. \quad (19b)$$

If we neglect the linear behavior and take an average over the measured range in q ($-1.3 < q < 5.4$ for the best data M_{NeAr}), we get

$$\bar{M}_{Ar} \cong 4.9D. \quad (19c)$$

Perhaps accidentally, these three values of \bar{M}_i vary monotonically with ρ_{ii} , and we find roughly that

$$(M_i / \rho_{ii} e) \approx 6, \quad (20)$$

where e is the electronic charge.

These rough estimates of atomic dipole moments are useful in predicting the effect of a dipole-dipole interaction term in the total repulsive potential. Clearly, the assumption that the repulsive energy is simply the sum of two distortion terms, one for each atom, as in Eq. (7), is not strictly correct. We must add a term of the form

$$V_\mu(r) = 2\mu_A(r_A)\mu_B(r_B)/r^3. \quad (21)$$

Using the relation

$$\mu_A(r_A) = M_A(q)e^{-q}, \quad (22)$$

TABLE II. Atomic distortion dipole moments. Data on μ , r reported in Ref. 24; values in parentheses calculated from the other data by the relationship $M_{HeNe} = M_{He} - M_{Ne}$.

$r(\text{He}_2)$ (a_0)	$r(\text{Ne}_2)$	q	μ_{He} (D)	μ_{Ne} (D)	M_{HeNe} (D)	M_{He} (D)	M_{Ne} (D)
4.98		8.23	0.00114		0.63	4.28	(3.65)
	5.20	6.66		0.00056	0.65	(1.10)	0.45
Average						2.69	2.05

this becomes

$$V_{\mu}(r) \cong 2M_A M_B e^{-2\alpha/r^3}. \quad (23)$$

This allows us to compare the distortion energy V_{dts} with the dipole-dipole energy V_{μ} . For example, when $V_{\text{dts}} = 0.1$ a.u., we find, roughly, that

$$V_{\mu}/V_{\text{dts}} \cong 0.5(\text{HeNe}), \quad 0.3(\text{HeAr}), \quad 0.2(\text{NeAr}). \quad (24)$$

Thus, the distortion energy should dominate over the interatomic electrostatic energy until the total potential is at least several eV.

This conclusion is reinforced by the fact that Eqs. (21) and (23) probably overestimate the interatomic electrostatic energy contribution. Since we are dealing with distributed electron clouds rather than point dipoles, higher multipole terms will partially cancel some of the apparent dipole-dipole energy, especially at small values of r . Another way to look at this is to note that the interatomic electrostatic contribution looks like Eq. (21) at intermediate r , then comes to look more like a pair of ion-dipole terms varying as r^{-2} , and finally like a shielded Coulomb term approaching r^{-1} behavior at small r . This gradual transition through the forms

$$Ae^{-\alpha r} \rightarrow Br^{-3}e^{-\beta r} \rightarrow Cr^{-2}e^{-\gamma r} \rightarrow Dr^{-1}e^{-\delta r} \quad (25)$$

may prove suggestive in finding an appropriate analytical form³⁰ that goes over from the exponential at large r to the screened Coulomb at small r (naturally, the effect of electronic shell structure must also be taken into account³¹).

Finally, it may be noted that when terms such as Eq. (21) are added to Eq. (7), it is still possible to minimize the total energy with respect to r_A and therefore determine a combining rule similar to but more complicated than Eq. (8). To apply it reliably, more information will be needed on the individual atomic dipole moments as a function of the distortion distance. Some empirical method

of treating the curvature of the distortion surface as it affects the atomic dipole moments may also be needed, when the atoms in collision differ greatly from each other in size or in tightness of binding.

Another effect of the atomic distortion caused by the Pauli exclusion principle is found in the alkali halide molecules, where the attractive force includes terms reflecting the polarization of each ion in the field of the other. Two distinct effects are to be expected: (a) The exclusion-principle distortion creates a dipole moment in each ion when the atoms are close together, which is different in nature from the electrostatic polarization caused by the ionic field of the other partner, and (b) the presence of the electron cloud of one ion restricts the electrostatic polarization of the other. Consequently, the distortion polarization and the electrostatic polarization are not independent, but both must be considered together. Their effects will be seen both in the molecular dipole moment and in the potential energy function. In the past, these polarization effects of distortion have not been adequately considered in the diatomic potential function, and the result has been a systematic discrepancy in the empirically evaluated repulsive energy term for the alkali halides when the diatomic molecules are compared with the crystals.^{27, 32}

In the future, I expect many useful applications of the distortion model, both in connection with electrostatic effects and in the combining rule for repulsive potentials. In particular, the study of the binding forces in clustered ions will give many opportunities for using and testing combining rules as they apply to closed-shell molecular species as well as atomic ones.³³ In neutral gases, Mason³⁴ has pointed out that the distortion dipole in a two-body collision will affect the interaction with a third body, and thereby contribute to non-additive effects in the intermolecular forces that are important in the third virial coefficient.

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PHYSICAL REVIEW A

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Relativistic Calculations for Photoionization Cross Sections and the Spin Orientation of Photoejected Electrons from Potassium, Rubidium, and Cesium Atoms*

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By using relativistic Hartree-Fock equations which automatically take the spin-orbit interaction into account, we calculate the single-particle states for photoejected electrons from heavy alkali-metal atoms. We derive an expression for the perturbation function x . Our results are in fair agreement with the experiments, but more accurate calculations including electron correlations are desirable.

INTRODUCTION

Recently, there has been considerable interest in the spin-orbit interaction in alkali-metal atoms.¹⁻⁴ As pointed out by Weisheit and Dalgarno,⁴ the spin-orbit interaction was used by Fermi⁵ in 1930 to explain the anomalous ²P line strength ratio in alkali-metal atoms. Seaton⁶ mentioned that the nonzero minimum of the photoionization cross sections of alkali-metal atoms is due to the spin-orbit interaction. Fano¹ has shown that the spin-orbit interaction for the valence electron of the alkali metals leads to a spin orientation of photoelectrons ejected by circularly polarized light. This spin orientation has been confirmed experimentally by Kessler and Lorenz² and by Baum, Lubell, and Raith.³

As shown by Fano, the degree of spin orientation is given by

$$P = (1 + 2x)/(2 + x^2), \quad (1)$$

where

$$x = [2R(\epsilon, \frac{3}{2}) + R(\epsilon, \frac{1}{2})] / [R(\epsilon, \frac{3}{2}) - R(\epsilon, \frac{1}{2})] \quad (2)$$

and

$$R(\epsilon, j') = \int_0^\infty P(\epsilon p j'; r) r P(ns \frac{1}{2}; r) dr. \quad (3)$$

In the above equation, $P(\epsilon p j'; r)$ is the radial part of the continuum wave function with energy ϵ , and $P(ns \frac{1}{2}; r)$ is the radial wave function for the valence ns electron.

Weisheit and Dalgarno calculated x for potassium by including a core-polarization correction which they obtained semiempirically by multiplying the operator \vec{r} with a function which contains the effective core radius r_c as an adjustable parameter. They also adopted the spin-orbit parameter $\xi(r) = 17.33/r^3$. By choosing $r_c = 4.22a_0$, where a_0 is the Bohr radius, their results for x are in excellent agreement with the experimental values. In this paper, we use relativistic Hartree-Fock (HF) equations to calculate the continuum wave functions and