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Exchange energy of alkali-metal dimer cations calculated from the atomic polarizability with the Holstein-Herring method

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A formula relating the dipole polarizability and the exchange energy is derived for alkali-metal dimer cations. The theory is based on the fact that the unsymmetrized polarized wave function gives both the polarizability and the exchange energy through the Holstein-Herring integral. The results are seen to be remarkably accurate for large interatomic distances.

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I. INTRODUCTION

The difference between the symmetrical (gerade) and antisymmetrical (ungerade) energy levels of a homonuclear molecule, which degenerate into a single atomic energy level when the internuclear distance becomes very large, is defined as the exchange energy. The exchange energy is of fundamental importance for understanding not only interatomic potentials, but also charge-exchange processes as well as the theory of magnetism. With ordinary quantum-chemistry methods, these energy levels are calculated separately and the exchange energy is obtained from the difference of two large numbers, resulting in a large relative error. The computational effort is usually very large, and results can be found in numerical form only. Even with modern methodology, it is still very difficult to obtain results of high accuracy, especially at large internuclear distances.

An alternative approach is to use the method of Holstein [1] and Herring [2], who expressed the exchange energy as a surface integral of the flux of the localized wave function of the electron. This method is straightforward for a one-electron system, but can be generalized to deal with more than one electron. If E_g and E_u are the eigenenergies corresponding to the gerade ψ_g and ungerade ψ_u eigenstates of the molecular system, respectively, the exchange energy defined as $\Delta E = E_u - E_g$ can be written for a molecular ion in the asymptotic region as

$$\Delta E = -2\int_M \Phi_a \nabla \Phi_a \cdot d\mathbf{s} \ , \tag{1}$$

where

$$\Phi_a = \frac{1}{\sqrt{2}}(\psi_g + \psi_u) \tag{2}$$

is the localized wave function centered around the nucleus a. The surface integral is over the median plane M at halfway between the nuclei. This formulation is appealing because it derives from the physical picture that the exchange energy is the energy of the electron oscillating between the two nuclei [1,3]. Moreover, it enables one to use atomic wave functions to calculate the molecular exchange energy. In the case of H_2^+, the exact asymptotic exchange energy can be expressed in an analytic form [2].

Recently, we have shown [3] that, in the asymptotic region, the required localized wave function in Herring's theory can be approximated by the polarized wave function obtained from the ordinary unsymmetrized Rayleigh-Schrödinger (RS) perturbation theory. Since the polarized wave functions are directly related to polarizabilities, this work suggests that it may be possible to express the exchange energy in terms of the polarizability.

In the present paper, we derive a simple formula for the asymptotic exchange energy of the H_2^+ molecular ion and the alkali-metal dimer cations based on an earlier calculation by Bardsley *et al.* [4]. In the present study, we show how the only undetermined parameter of their expression can be related to the dipole polarizability. This leads to an asymptotic formula relating the exchange energy to the dipole polarizability of the isolated atoms. In the case of H_2^+, the result is exact. For alkali-metal dimer ions, for which the exact atomic wave functions are not available, our results agree well with the best recently available *ab initio* calculations, indicating that the present method is efficient and remarkably accurate. Atomic units are used throughout this paper.

II. HOLSTEIN-HERRING THEORY FOR ALKALI-METAL DIMER IONS

In this section we will give a short review of the calculation of Bardsley *et al.* [4], who applied the theory of Holstein to the alkali-metal dimer ions.

The electronic structure of the alkali-metal dimer ions is approximated by assuming that they consist of two positively charged inert cores (nuclei and inner electrons) and one valence electron. In the coordinate system shown in Fig. 1, the vectors $\mathbf{r}_a$ and $\mathbf{r}_b$ denote the position of the electron with respect to the cores at a and b. The interatomic distance is given by R. Since we are using the Born-Oppenheimer approximation, the calculated energies will have only a parametric dependence on R. M is the median plane between and a and b.

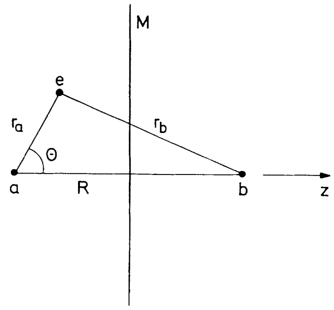

FIG. 1. Coordinates of the electron e and ion cores a and b used in the present model calculation of the exchange energy. M is the median plane located halfway between the cores.

A. Approximation for the atomic wave function

In order to calculate the exchange energy from the flux of the electrons, the atomic wave functions need to be approximated. For the hydrogen atom, the wave function is, of course, exact. For the alkali-metal atoms, we will assume that the spatial part of the wave function can be written as a product of the wave functions for the positive-ion core and the valence electron. The difference between the orbital energies of the core and valence electron is relatively high for the alkali metals (e.g., 62.1 eV for lithium between the $2s$ and a $1s$ electron), and so this is a reasonable assumption. According to Koopmann's theorem, the ionization energy ε is the orbital energy of the outer electron. Thus the wave function of the valence electron ψ_0 has to be a solution of the equation

$$[-\tfrac{1}{2}\nabla^2+V_0(r)+\varepsilon]\psi_0(r)=0 , \tag{3}$$

where $V_0(r)$ is the effective potential of the core, as determined, for example, from a Hartree-Fock self-consistent-field calculation. An explicit form of ψ_0 can be derived in the long-range asymptotic region, where $V_0(r)\approx -1/r$. In this region, ψ_0 can be approximated by a generalized s orbital [4]:

$$\psi_0(r)\approx \frac{q}{\sqrt{4\pi}}\left[1+\frac{p}{r}\right]r^{1/\beta-1}e^{-\beta r} . \tag{4}$$

It can be shown by direct substitution that this is indeed a solution of Eq. (3) if terms of order $O(1/r^3)$ are neglected. Moreover, it is found that

$$\beta=\sqrt{2\epsilon},\quad p=-\frac{1}{2\beta^2}\left[\frac{1}{\beta}-1\right] . \tag{5}$$

Thus β and p are both determined by the ionization energy ϵ. The amplitude of $\psi_0(r)$, q, is however not determined by this procedure. Note that q cannot be simply calculated by setting $\langle\psi_0|\psi_0\rangle=1$, since Eq. (4) is not a valid wave function at small distances, where the effect of the finite size of the core cannot be neglected.

B. Calculation of the exchange energy

In the calculation of the exchange energy from Eq. (1), it is necessary to have an expression for the localized wave function Φ_a. As Herring [2] showed, Φ_a can be approximated by the atomic wave function χ_a, which satisfies the equation

$$\left[-\frac{1}{2}\nabla^2+V_0(r_a)-\frac{1}{r_b}+\frac{1}{R}+\epsilon'\right]\chi_a=0 , \tag{6}$$

on the left-hand side of M, i.e., in the half space containing atom a. The terms $1/r_b$ and $1/R$ account for the perturbation produced by the ion core at b, and ϵ' is the new energy of the perturbed atom. Bardsley *et al.* [4] used the WKB approach and expressed χ_a as

$$\chi_a(\mathbf{r}_a)=\psi_0(r_a)e^{-S_1-S_2-\cdots} , \tag{7}$$

where S_1 and S_2 are successively higher orders of $1/R$. They found

$$S_1=\frac{1}{\beta}\left[\frac{r_a}{R}-\ln\left[\frac{r_a+r_b-R\cos\theta_a}{R(1-\cos\theta_a)}\right]\right] , \tag{8}$$

$$\begin{aligned}S_2=\frac{1}{\beta^2 R}\Bigg[&\ln\left[\frac{R+r_a+r_b}{2R}\right]+\ln\left[\frac{R+r_b-r_a}{2R}\right]\\&+\left[\frac{1}{\beta}-1\right]\ln\left[\frac{r_b+R-r_a\cos\theta_a}{2R}\right]\Bigg]\\&-\frac{1}{\beta^3 R}\left[\frac{r_a}{2R}-\ln\left[\frac{R+r_a+r_b}{R+r_b-r_a}\right]\right.\\&\left.+\frac{R}{R+r_b-r_a}-\frac{R}{R+r_b+r_a}\right] .\end{aligned} \tag{9}$$

Note that S_1 and S_2 become zero if either r_a approaches zero or as R approaches infinity, so that in these cases $\chi_a(\mathbf{r}_a)$ reduces to $\psi_0(r_a)$ of Eq. (4). Substituting Eq. (7) for Φ_a and performing the surface integral (1), the exchange energy is found to be [4]

$$\begin{aligned}\Delta E(R)=\pi R\left[\frac{4}{e}\right]^{1/\beta}\psi_0^2\left[\frac{R}{2}\right]\Bigg[&1+\frac{1}{\beta^2 R}\left[\frac{3}{2\beta}-1\right]\\&+O\left[\frac{1}{R^2}\right]\Bigg] .\end{aligned} \tag{10}$$

The first two terms of the exchange energy are uniquely determined, provided that the wave function ψ_0 and parameter β of the single atom are known.

III. DEPENDENCE OF THE EXCHANGE ENERGY ON THE ATOMIC POLARIZABILITY

The only unknown parameter in the calculation of the exchange energy by Eq. (10) is the amplitude q of the one-electron wave function ψ_0. Bardsley *et al.* [4] suggested different methods for the derivation of q, all based on a fit to an atomic self-consistent-field (SCF) calculation or a pseudopotential calculation. The method we are going to present here will relate q to the atomic polarizability, which is a straightforward way of treating the problem, and no fitting will be required.

Recently, we have shown [3] that the localized wave function χ_a can be calculated from unsymmetrized Rayleigh-Schrödinger perturbation theory. Thus χ_a can be expanded as

$$\chi_a = \psi_0(r_a) + \psi_1(\mathbf{r}_a) + \psi_2(\mathbf{r}_a) + \cdots , \tag{11}$$

where the $\psi_n(\mathbf{r}_a)$ are the nth order perturbed wave functions. These wave functions ψ_n are governed by the hierarchy of the perturbation equations

$$\begin{aligned} &(H_0 - \varepsilon_0)\psi_0 = 0 \quad (n=0) , \\ &(H_0 - \varepsilon_0)\psi_1 + (V - \varepsilon_1)\psi_0 = 0 \quad (n=1) , \\ &(H_0 - \varepsilon_0)\psi_n + (V - \varepsilon_1)\psi_{n-1} = \sum_{k=2}^{n} \varepsilon_k \psi_{n-k} \quad (n \geq 2) , \end{aligned} \tag{12}$$

where $\varepsilon_{n+1} = \langle \psi_n | V | \psi_0 \rangle$. Furthermore, the perturbing potential in the asymptotic region is replaced by its multipole expansion

$$V = -\sum_{l=1}^{\infty} \frac{r^l}{R^{l+1}} P_l(\cos\theta) , \tag{13}$$

where $P_l(\cos\theta)$ is the Legendre polynomial.

It is clear from Eq. (12) that all higher-order perturbed wave functions depend on the zeroth-order wave function. If ψ_0 can be determined only up to a constant, then all higher orders ψ_n can only be determined up to that same constant. Thus, if this constant is determined for any order of ψ_n, it is determined for all. We observe that if the first-order wave function ψ_1 of Eq. (11) is expressed in a multipole expansion, the leading term is exactly the polarized wave function due to the perturbation of a constant field, the second term is the polarized wave function due to a constant field gradient dE/dR, etc. Therefore ψ_1 must be related to the dipole polarizability α_d. It turns out that the amplitude of ψ_1 can, in fact, be determined directly from the dipole polarizability. Then, using the relationship between ψ_0 and ψ_1, we can also determine the amplitude of ψ_0. Quantitatively, this can be seen as follows.

The leading term of Eq. (13) is

$$V_{l=1} = -\frac{r\cos\theta}{R^2} = -\frac{z}{R^2} , \tag{14}$$

where z is in the direction of the internuclear axis. The electron of atom a is therefore pulled to one side by a force

$$F_z = -\frac{\partial V_1}{\partial z} = \frac{1}{R^2} . \tag{15}$$

It is important to note that F_z does not depend on either r or θ. The polarization of the wave function due to this perturbation is therefore the same as if the atom were placed in a constant electrical field E in the z direction with a field strength of $-1/R^2$. The polarized wave function and the perturbed energy of the atom a in the field of the ion at b can be calculated by the variation principle.

The Hamiltonian of the system with the leading term of Eq. (13) is given by

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r} + Ez . \tag{16}$$

The trial function

$$\psi_t = \psi_0[1 + r\cos(\theta)(A + rB)] , \tag{17}$$

with ψ_0 from Eq. (4) and A and B as variation parameters, gives the *exact* energy up to second order in the case of hydrogen [5]. Thus we can expect good results for the alkali-metal atoms as well. For this case the parameters are determined by minimizing the expectation value for the energy

$$\mathcal{E} = \frac{\langle \psi_t | H | \psi_t \rangle}{\langle \psi_t | \psi_t \rangle} . \tag{18}$$

Assuming the field to be small, only the linear term of E in the variation parameters is considered. That is, $A = A'E$ and $B = B'E$. This variational procedure gives directly the values of A' and B'. Note that, if ψ_t is exact in first order, the calculated energy will be exact up to second order.

The induced electric dipole moment corresponding to ψ_t is given by

$$\mu = -\langle \psi_t | z | \psi_t \rangle . \tag{19}$$

We know also that the induced dipole moment is proportional to the electric field:

$$\mu = \alpha_d E , \tag{20}$$

where α_d is the dipole polarizability. Substituting Eq. (17) with ψ_0 given by Eq. (4) into Eq. (19), we find after some computation that

$$-\langle \psi_t | z | \psi_t \rangle = q^2 E K , \tag{21}$$

with

$$K = -\tfrac{2}{3}\int_0^\infty \left[1 + \frac{p}{r}\right]^2 (A' + rB') r^{2/\beta+2} e^{-2\beta r} dr . \tag{22}$$

Combining Eqs. (19)–(21), we obtain finally a simple expression for the unknown amplitude q of Eq. (4):

$$q = \left[\frac{\alpha_d}{K}\right]^{1/2} . \tag{23}$$

The dipole polarizability of the charge distribution represented by ψ_0 can also be calculated from the result of the variational calculation. The variational energy $\mathcal{E}$ is obtained as a polynomial in the field strength E, where the dipole polarizability is proportional to the second-order term

$$\mathcal{E}_2 = -\tfrac{1}{2}\alpha_d' E^2 . \tag{24}$$

This value for the dipole polarizability α_d' can also be used in Eq. (23) for calculating the amplitude. We will denote the result as q' and see in Sec. IV that the difference between the two values is small.

IV. RESULTS AND DISCUSSION

The variational calculation was performed analytically by a REDUCE [6] routine. The results for A' and B' are shown in Table I for all the alkali-metal dimer ions and the hydrogen molecule ion. The values of β which are calculated from the ionization energies by Eq. (5) and the "best" literature values [8] of the dipole polarizabilities α_d are also shown in Table I.

The calculated energy has a constant term which is equal to ϵ, because ψ_t is an eigenfunction of H in zeroth order. There is no linear term in E, which means that the perturbation energy is not dependent on the sign of the field or, in other words, that there is no permanent electric dipole moment when the perturbation vanishes. Thus the second-order term $\mathcal{E}_2 = -1/2\alpha_d' E^2$ becomes the lowest order of the perturbation energy. We checked the stability of $\mathcal{E}_2$ with respect to the form of the trial wave function by introducing a third variational parameter C. The modified trial function is

$$\psi_t' = \psi_0[1 + r\cos(\theta)(A + rB + r^2 C)] \ . \tag{25}$$

The results for the perturbed lithium atom are

$$\mathcal{E}_2 = -70.20E^2 \quad [\text{Eq.}(17)] \ ,$$

$$\mathcal{E}_2 = -70.85E^2 \quad [\text{Eq.}(25)] \ .$$

The energy difference is only 0.9%. Therefore Eq. (17) seems to be an adequate description of the field-induced distortion. The values for α_d' and their deviation from the "exact" values are also given in Table I, together with the constant q and q' calculated by Eq. (23) from these two different values of the dipole polarizability. The values of q and q' decrease in going from H to Cs. This can be explained by noting that for the bigger atoms the valence electron is distributed over a wider region, corresponding to a smaller amplitude of the wave function.

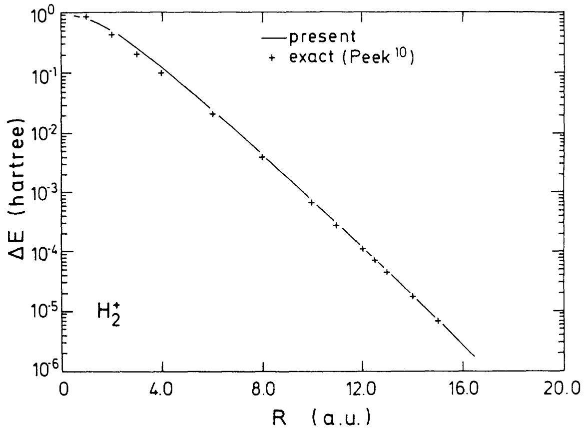

FIG. 2. ΔE for $H_2{}^+$. The calculated expression is identical with the exact asymptotic exchange energy [1]. Compared with the exact results of Peek [10], the relative error at $R = 15$ a.u. is only 0.7%.

For hydrogen, the calculated polarizability is exact, but for the alkali-metal atoms, with the exception of Li, the percentage error increases with the size of the atom. This can be explained by recalling that the calculation is based on two fundamental approximations. First, the polarizability of the core electrons is neglected. Therefore the calculated value should be *too small.* This is the case only for lithium, which has only a very small core polarizability, and so there must be another competing effect for the larger atoms. It comes from the second approximation, which assumes the core potential to be $1/r$. This is correct only in the case of a perfect screening of the nuclear charge by the inner electrons. But the charge density in the outer closed shells becomes more diffuse in going from Li to Cs. As a consequence, the *effective* core potential "seen" by the outer electron tends to be *larger* than $1/r$. In this case the attractive force on the valence electron is greater and this reduces its polarizability. Therefore neglecting this effect will give *too large* a value for α_d', which is indeed the case for the heavier alkali-metal atoms. In principle, this error could be reduced by the use of an effective core potential instead of $V_0 = -1/r$ in Eq. (3). For example, Chang *et al.* [9] used a potential of the form

$$V_0 = -\frac{1}{r} - \frac{n}{r} e^{-\gamma r} \ , \tag{26}$$

TABLE I. Results of the variatonial calculation. Using the ionization energy ε, the variational parameters A' and B' are calculated. These values and the dipole polarizability α_d (α_d') are used to calculate the amplitude q (q').

System	ε (Hartree)[a]	β[b]	$\alpha_d(a_0^3)$[c]	A'[d]	B'[d]	$\alpha_d'(a_0^3)$[e]	q[f]	q'[g]
H	−0.500 00	1.000 00	4.5	−1.00	−0.500	4.5 (±0.0%[h])	2.000	2.000
Li	−0.196 32	0.626 61	164.3	−11.35	−0.124	140.4 (−14.5%)	0.858	0.793
Na	−0.188 86	0.614 59	162.6	−12.49	−0.084	163.3 (+0.43%)	0.747	0.749
K	−0.159 50	0.564 80	298.0	−18.53	−0.090	314.7 (+5.62%)	0.554	0.569
Rb	−0.153 50	0.554 08	330.0	−20.14	−0.125	364.8 (+10.53%)	0.505	0.531
Cs	−0.143 10	0.534 98	416.5	−23.25	−0.175	476.4 (+14.39%)	0.436	0.466

[a] Ionization energy [7].
[b] Calculated by Eq. (5).
[c] Dipole polarizability [8].
[d] Optimized variational parameters.
[e] Dipole polarizability calculated by Eq. (24).
[f] Amplitude calculated by Eq. (23) using α_d.
[g] Amplitude calculated by Eq. (23) using α_d'.
[h] Error relative to α_d (column 4).

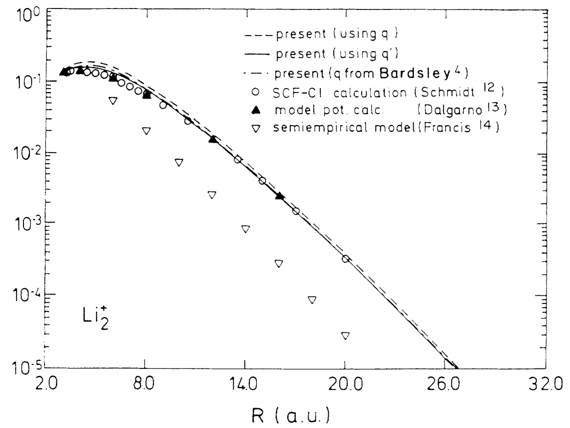

FIG. 3. ΔE for Li_2^+. The present results using q (from exact α) and q' (from calculated α) are compared with the values of Bardsley *et al.* [4] [Eq. (10) with their q], Schmidt [12] [SCF plus configuration-interaction (SCF/CI) calc.], Bottcher, Allison, and Dalgarno [13] (model pot. calc.) and Francis and Rapp [14] (semiempirical model).

where n and γ are adjustable parameters that can be determined by a fit to spectroscopic data. Unfortunately, Eq. (26) cannot be applied in a straightforward manner since it does not lend to a closed form of the one-electron wave function ψ_0, which is required in order to carry out a WKB calculation similar to the approach of Bardsley *et al.* [4].

Figures 2–7 compare the exchange energy calculated by Eq. (10) with different *ab initio*, model, and pseudopotential calculations for H_2^+ and the alkali-metal dimer ions. The excellent agreement in the case of H_2^+ (Fig. 2) was already noted in an earlier closely related calculation [11]. Figure 3 shows a comparison of the exchange energy calculated with q and q' for Li_2^+. The agreement with the best *ab initio* potentials [12] in the asymptotic region is very good. It is slightly better using q' instead of q. This is an additional justification for neglecting the core, because q' is calculated from α_d', which is the calculated polarizability of the one-electron function ψ_0. It is in any case a more consistent way of treating the problem, because in the derivation of Eq. (1) for ΔE we also assumed that the core can be neglected. For Li_2^+ we also compare our results with the curve obtained from Eq. (10) by using the best q value of Bardsley *et al.* [4]. One can see that our results using q' are in better agreement with the *ab initio* data. For example, at $R=20$ a.u., the deviation of ΔE calculated with q' from the *ab initio* value is $+2.0\%$. Using the q value of Bardsley *et al.* [4] the deviation is $+7.5\%$. Figure 4 shows the comparison for Na_2^+. The agreement between the present results and the best *ab initio* calculation [12] is also very good.

For the heavier alkali metals shown in Fig. 5–7, no *ab initio* potential curves are available and the present results can only be compared with various approximations.

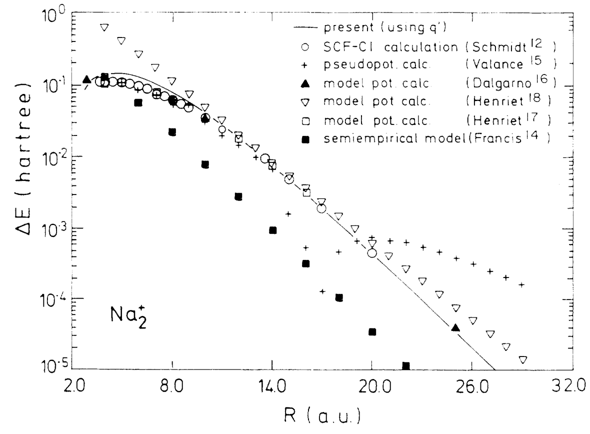

FIG. 4. ΔE for Na_2^+. The present results using q' from calculated α are compared with earlier calculations of Schmidt [12] [(SCF-CI) calc.), Valance [15] (pseudopot. calc.) Cerjan, Docken, and Dalgarno [16] (model pot. calc.), Henriet [17], Henriet and Masnou-Seeuws [18] (model pot. calc.), and Francis and Rapp [14] (semiempirical model).

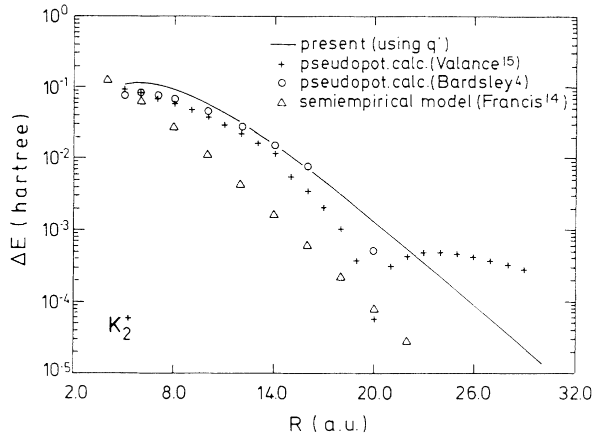

FIG. 5. ΔE for K_2^+. The present results using q' from calculated α are compared with earlier calculations of Valance [15] (pseudopot. calc.), Henriet [17] (model pot. calc.), and Francis and Rapp [14] (semiempirical model).

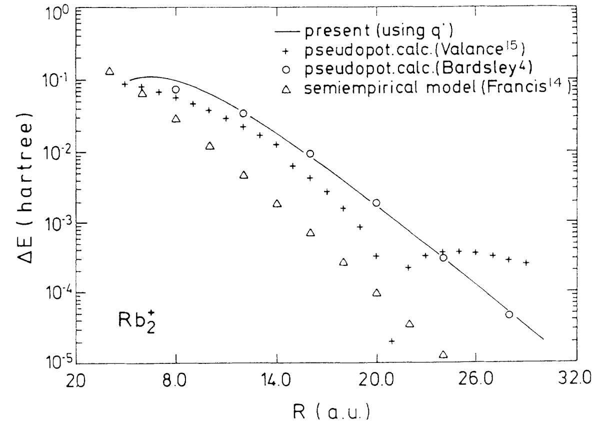

FIG. 6. ΔE for Rb_2^+. The present results using q' from calculated α are compared with earlier calculations of Valance [15] (pseudopot. calc.), Bardsley [19] (pseudopot. calc.), and Francis and Rapp [14] (semiempirical model).

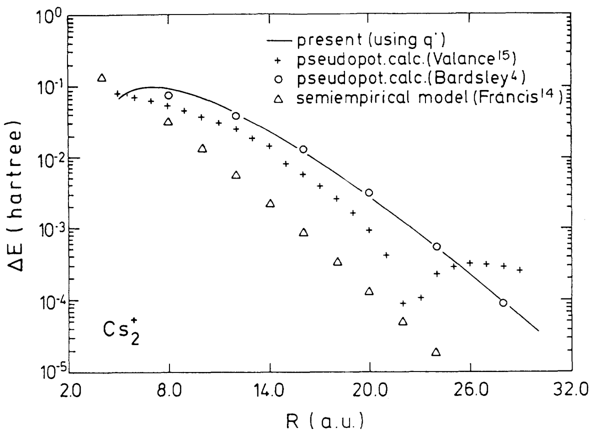

FIG. 7. ΔE for $Cs_2{}^+$. The present results using q' from calculated α are compared with earlier calculations of Valance [15] (pseudopot. calc.), Bardsley [19] (pseudopot. calc.), and Francis and Rapp [14] (semiempirical model).

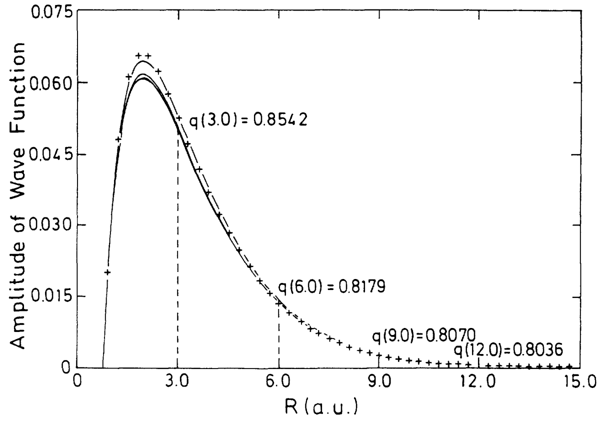

FIG. 8. Comparison of wave functions for the valence electron of lithium. Crosses: SCF calculation with a basis set of six slater orbitals (Clementi and Roetti [21]). Lines: four different fits of Eq. (4) of the present paper. The amplitude q is chosen by fitting ψ_0 to the SCF data at different distances.

Francis and Rapp [14] were the first to derive a simple approximate formula for the exchange energy. Using a semiempirical model, they found

$$\Delta E = 2\epsilon R e^{-\beta R}\ , \tag{27}$$

where ϵ is the effective ionization energy of the atom [see Eq. (3)] and β is given by Eq. (5). As can be seen in Figs. 3 and 4, this simple expression is in poor agreement with the *ab initio* calculations for $Li_2{}^+$ and $Na_2{}^+$. Thus this expression probably is also not reliable for the heavier systems. The pseudopotential calculations of Valance [15] for $Na_2{}^+$, $K_2{}^+$, $Rb_2{}^+$, and $Cs_2{}^+$ have a much different shape in the asymptotic region, which is probably caused by a lack of numerical accuracy of their potential curves for the ${}^2\Sigma_g^+$ and ${}^2\Sigma_u^+$ states at large internuclear distances. Thus the relatively large error comes from subtracting two nearly equal large values. For $Li_2{}^+$ and $Na_2{}^+$, the model potential calculations of Dalgarno and coworkers [13,16] are in very good agreement with the present results. The only reliable data for $Cs_2{}^+$ and $Rb_2{}^+$ are the pseudopotential calculations of Bardsley [19]. The agreement in the asymptotic region is very good for these systems. For potassium, only the calculations of Valance [15] and Francis and Rapp [14] are available at large distances. In view of the large deviations of these calculations for the other systems, the present results are probably the most reliable for the potassium dimer ion.

Previously, both Smirnov and Chibisov [20] and Bradsley *et al.* [4] have proposed to determine q by fitting ψ_0 to the wave function obtained by a SCF calculation. In Fig. 8 we show such a fit for the lithium dimer ion using the SCF data of Clementi and Roetti [21]. Although the general shapes of ψ_0 of Eq. (4) and the SCF curve are reasonably close, they are not identical. For this reason the fit is not unique and the dependence of q on the distance where the fit is made is still considerable. It varies from $q = 0.85$ for $r = 3$ a.u. to $q = 0.80$ for $r = 12$ a.u., which is to be compared with our result of $q = 0.793$. The present method is more direct, and since it does not depend on the SCF data, it is internally more consistent.

Probably, the most important result of the present investigation is the observation that the exchange energy is related to the polarizability. The explicit relation between the dipole polarizability α_d and the exchange energy ΔE derived from Eqs. (4), (10), and (23) is

$$\Delta E(R) = \frac{\alpha_d}{K} R^{2/\beta - 1}\left[1 + \frac{2p}{R}\right]^2 e^{-\beta R - 1/\beta} \times \left[1 + \frac{1}{\beta^2 R}\left[\frac{3}{2\beta} - 1\right] + O\left[\frac{1}{R^2}\right]\right]\ , \tag{28}$$

where β and p are determined by Eq. (5) and K by Eq. (22). Since K does not depend on α_d, the exchange energy is directly proportional to α_d. The dependence on the ionization energy is more complicated since K, β, and p are all functions of ϵ. With Eq. (28) it is possible to calculate simply and analytically the exchange energy for any of the alkali-metal dimer ion systems.

V. CONCLUSIONS

The advantage of the present procedure compared with other methods lies in the direct derivation of the exchange energy without the need of any fitting to other complicated calculations. The present model provides an explicit relationship between molecular-ion exchange energies and the properties of the atoms. It is interesting to note that recently, Liuti and co-workers [22,23] have discovered an empirical quantitative relationship between the polarizability of the single atom and the well depth and its location of the van der Waals potential for a number of diatomic systems.

In the future we hope to be able to derive a simple expression for the entire potential curve in terms of the properties of the atomic constituents. At least for the alkali-metal dimer ions, such an expression now seems within reach. As is well known, the total interaction energy can be written as [24]

$$V(^2\Sigma_g^+)=V_{\text{Coul}}-\tfrac{1}{2}\Delta E \ , \tag{29}$$

$$V(^2\Sigma_u^+)=V_{\text{Coul}}+\tfrac{1}{2}\Delta E \ , \tag{30}$$

where V_{Coul} is the Coulomb energy. This can be considered to consist of two terms: the first-order Coulomb energy $V_{\text{Coul}}^{(1)}$, which can be calculated using standard SCF procedures, and the second-order induction and dispersion energy $V_{\text{Coul}}^{(2)}$ [25]. The latter can be accurately approximated from the results of a perturbation theory calculation, and for the present system, it is dominated by the induced dipole term, which is also proportional to the dipole polarizability α_d. In the region of the van der Waals minimum ($^2\Sigma_u^+$ minimum), the first-order Coulomb energy is probably much smaller than other components. Thus the van der Waals potential may indeed be dominated by terms which are directly related to the polarizability.

In principle, the present method should be applicable to all systems that have the required symmetry which causes the degeneracy of the molecular states at large interatomic distances. This is the basis for the present definition of the exchange energy. If we consider systems with n valence electrons, the integral in Eq. (1) is over $(3n-1)$-dimensional hypersurface. Therefore the analytical effort to carry out this integral as well as the problem of finding an approximate localized n-electron wave function increases considerably with the complexity of the system. The derivation of an expression for the exchange energies of H_2 and the neutral alkali-metal dimers is in progress.

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