

Calculations of ion-atom interactions relating to resonant charge-transfer collisions*

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The interaction between an atom and ion of the same element leads to gerade and ungerade states of the diatomic molecular ion. The energy splittings between the gerade and ungerade states determine the cross section for resonant charge transfer. Using the JWKB approach these energy splittings are derived from the asymptotic forms of the wave functions for the isolated atom and ion. Pseudopotential calculations of the splittings are reported for Li_2^+ , Na_2^+ , Rb_2^+ , and Cs_2^+ , and are used together with previous *ab initio* and model-potential calculations to test the JWKB method. The comparison shows that the method is sufficiently reliable to facilitate accurate calculations of the cross sections for resonant charge transfer at low energies.

I. INTRODUCTION

The cross sections for charge transfer at low energies in the collision of an ion X^+ or X^- with the corresponding neutral atom X are determined mainly by the potential curves of the low-lying states of the molecule, X_2^+ or X_2^- , which is formed temporarily during the collision. The crucial feature which controls the cross section is the difference between the energies of these states.¹⁻⁵ For collisions at thermal energies the long-range interactions, with say $R \gtrsim 10a_0$, are of great importance. At such separations the energy splittings are very small and it is difficult to perform *ab initio* calculations with sufficient accuracy to obtain reliable cross sections.

In 1952 Holstein⁴ suggested that these energy differences could be calculated analytically by a technique based on the JWKB approach. Some details of this method were presented in an unpublished report in 1955,⁶ and the method has been applied by several authors, principally by Smirnov and collaborators.⁷⁻¹² The purpose of this work is to obtain a generalized version of Holstein's theory and to assess its accuracy, by comparison with *ab initio* and pseudopotential calculations.

In this paper we will restrict our attention to positive ions, and will use a one-electron model. This model, which will be described later, is directly applicable to all atoms with completely filled subshells, such as the inert-gas and alkaline-earth atoms, and to those with a singly occupied open

shell, such as the alkali atoms, boron, and aluminum. We will also neglect the effects of spin-orbit interactions.

The aim of the theory, which is described in Secs. II, IV, and V, is to relate the energy difference between the gerade and ungerade states of the molecule X_2^+ to the asymptotic form of the wave function of the isolated neutral atom. If this asymptotic form is known, then the computation can be completed without the aid of a computer. In Secs. II and III we study the simplest systems with a single valence electron which is in an s orbital in the separated neutral atom. In Sec. IV we study atoms such as He, with two s -wave electrons in the outer shell. We will try to clarify some of the confusion that has existed in the literature regarding the effects of the indistinguishability of the electrons in such atoms. In Sec. V we will consider atoms in which the outer electron has nonzero angular momentum. In this paper we confine our attention to positive ions. Negative ions will be treated by the same technique in a forthcoming publication.

The size of the energy splittings at a given value of the internuclear distance is strongly correlated to the atomic ionization potential and may change by many orders of magnitude as one goes from Cs to He. Previous theories²⁻⁸ have demonstrated that the dependence of the cross section upon the energy splitting is logarithmic. This slow variation means that calculation of the energy splittings with an error of, say, 20 to 30%, can lead to ac-

curate predictions of cross sections. However, we will show that overly crude models can lead to errors which are much larger than this.

Atomic units will be used throughout this paper.

II. BASIC THEORY

In this paper we will assume that the spatial part of the wave function for the neutral atom in the asymptotic region in which one electron is far from the nucleus can be written as the product of the wave function for the positive ion and an additional orbital. This assumption is clearly valid for the alkali-metal atoms. In this section we study the interaction between an atom X , which possesses a single valence electron in an s orbital, and the corresponding ion X^+ at a distance R . We will further assume that in the isolated atom X the valence electron can be described by a wave function $u_0(r)$, which is the solution of an equation

$$[-\frac{1}{2}\nabla^2 + V_0(r) + \epsilon]u_0(r) = 0. \quad (1)$$

In this equation $V_0(r)$ could represent the Hartree-Fock self-consistent field, or it could be an empirical model potential or pseudopotential. The binding energy of the valence electron is denoted by ϵ . We will need an explicit form for $u_0(r)$ only in the asymptotic region, in which $V_0(r) = -1/r$. In this region we can expand $u_0(r)$ in inverse powers of r

$$u_0(r) \approx \frac{q}{\sqrt{4\pi}} \left(1 + \frac{p}{r} + \dots\right) r^{\nu-1} e^{-\zeta r}. \quad (2)$$

Only the first two terms in this series will be needed in our analysis. By substitution into Eq. (1) we obtain the relations

$$\zeta = (2\epsilon)^{1/2}, \quad \nu = 1/\zeta \text{ and } p = -\frac{1}{2}\nu^2(\nu - 1). \quad (3)$$

ν is the effective principal quantum number, which is often denoted by n^* . Our discussion of the choice of the constant q will be deferred until later.

Let us suppose that the two nuclei are at A and B , and let \vec{r}_a and \vec{r}_b represent the position of the electron relative to A and B , as shown in Fig. 1.

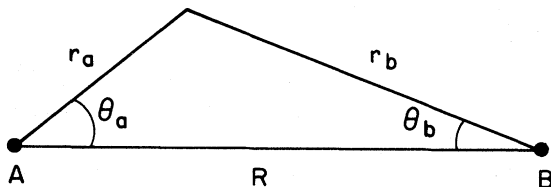


FIG. 1. Coordinate system used for molecular ions with a single valence electron. The two nuclei are at A and B .

The wave function for the valence electron can be written

$$\psi_{\pm}(\vec{r}) = N_{\pm} [u(\vec{r}_a) \pm u(\vec{r}_b)], \quad (4)$$

depending upon the desired symmetry of the molecular orbital. Our aim is to determine the difference in the energies of the two states $\psi_{\pm}(\vec{r})$. The function $u(\vec{r}_b)$ can be obtained from $u(\vec{r}_a)$ by reflection in the median plane. Note that for Σ states this implies that ψ_+ and ψ_- possess, respectively, gerade and ungerade symmetries with respect to inversion.

The functions $u(\vec{r}_a)$ and $u(\vec{r}_b)$ can strictly be defined only from the molecular states, using Eq. (4). However, our first step is to assume that the function $u(\vec{r}_a)$ represents the wave function for the valence electron in an atom, centered at A , which is distorted by the presence of an ion at B . We compute this wave function only in the half of space for which $r_a < r_b$. At such points we know that $r_b > \frac{1}{2}R$, and we assume that R is sufficiently large that the interaction of the valence electron with the ion at B can be approximated by $-1/r_b$. We then express $u(\vec{r}_a)$ in the form

$$u(\vec{r}_a) = u_0(r_a)v(\vec{r}_a) = u_0(r_a) \exp(-S_1 - S_2 - \dots) \quad (5)$$

in which S_1, S_2 are of successively higher order in $1/R$. The change in the energy of the atom due to the presence of the ion is of order $1/R^4$, and in the calculation of S_1 and S_2 this change can be neglected. We therefore demand that

$$[-\frac{1}{2}\nabla^2 + V_0(r_a) - 1/r_b + 1/R + \epsilon]u(\vec{r}_a) = 0. \quad (6)$$

Substituting (5) into (6), with a change of sign, we obtain

$$\begin{aligned} \frac{1}{2}u_0(r_a)\nabla^2 v(\vec{r}_a) + \nabla u_0(r_a) \cdot \nabla v(\vec{r}_a) \\ = (1/R - 1/r_b)u_0(r_a)v(\vec{r}_a). \end{aligned} \quad (7)$$

In our further development we will need to know the behavior of $u(\vec{r})$ for points close to the median plane between the nuclei. Thus we will regard $1/r_a, 1/r_b$, and $1/R$ as being of the same order of magnitude. To first order we find

$$\zeta \left(\frac{\partial S_1}{\partial r_a} \right) u_0(r_a) e^{-S_1} = \left(\frac{1}{R} - \frac{1}{r_b} \right) u_0(r_a) e^{-S_1}. \quad (8)$$

In deriving this result we have assumed that $(\partial^2 S_1 / \partial r_a^2)$ is of higher order than $\partial S_1 / \partial r_a$, and later we will make a similar assumption concerning

S_2 . These assumptions can be verified from the expressions for S_1 and S_2 that are presented below.

Using polar coordinates, as shown in Fig. 1, Eq. (8) has the solution

$$S_1 = \frac{1}{\xi} \left[\frac{r_a}{R} - \ln \left(\frac{r_a + r_b - R \cos \theta_a}{R(1 - \cos \theta_a)} \right) \right]. \quad (9)$$

Equation (8) would, in general, permit the addition to $S_1(\vec{r})$ of an arbitrary function of θ . This function is eliminated by the requirement that as $r_a \rightarrow 0$,

$$S_2 = \frac{1}{\xi^2 R} \left[\ln \left(\frac{R + r_a + r_b}{2R} \right) + \ln \left(\frac{R + r_b - r_a}{2R} \right) + (\nu - 1) \ln \left(\frac{r_b + R - r_a \cos \theta_a}{2R} \right) \right] - \frac{1}{\xi^3 R} \left[\frac{r_a}{2R} - \ln \left(\frac{R + r_b + r_a}{R + r_b - r_a} \right) + \frac{R}{R + r_b - r_a} - \frac{R}{R + r_b + r_a} \right]. \quad (11)$$

By combining Eqs. (4), (5), (9), and (11) we now have approximations to the molecular orbitals $\psi_i(\vec{r})$ which are accurate except when the valence electron is close to either of the nuclei. Let us now examine more closely the energies, $E_+(R)$ and $E_-(R)$, associated with these orbitals. Let us apply Green's theorem to the region of space \mathcal{L} in which $r_a < r_b$. Denoting the median plane by \mathfrak{M} , and the associated normal derivative by $\partial/\partial n$, we obtain

$$2[E_-(R) - E_+(R)] \int_{\mathcal{L}} \psi_+(\vec{r}) \psi_-(\vec{r}) d\tau = - \int_{\mathfrak{M}} \left(\psi_+(\vec{r}) \frac{\partial}{\partial n} \psi_-(\vec{r}) - \psi_-(\vec{r}) \frac{\partial}{\partial n} \psi_+(\vec{r}) \right) ds. \quad (12)$$

In terms of the distorted atomic orbitals $u(\vec{r}_a)$ and $u(\vec{r}_b)$, this equation becomes

$$[E_-(R) - E_+(R)] \int_{\mathcal{L}} [u^2(\vec{r}_a) + u^2(\vec{r}_b)] d\tau = - \int_{\mathfrak{M}} \left(u(\vec{r}_b) \frac{\partial}{\partial n} u(\vec{r}_a) - u(\vec{r}_a) \frac{\partial}{\partial n} u(\vec{r}_b) \right) ds. \quad (13)$$

Using the symmetry of $u(\vec{r}_a)$ and $u(\vec{r}_b)$ we can write

$$\Delta E(R) = E_-(R) - E_+(R) = -2 \int_{\mathfrak{M}} u(\vec{r}_a) \frac{\partial}{\partial n} u(\vec{r}_a) ds / \int u^2(\vec{r}_a) d\vec{r}_a \quad (14)$$

in which the volume integral is evaluated over all space. Retaining terms of order $1/R$, the normal derivative at points on the median plane is given by

$$\frac{\partial}{\partial n} u(\vec{r}_a) = -u(\vec{r}_a) [\xi \cos \theta (1 - 1/\xi^2 R) - (2/R)(\nu - 1) \cos^2 \theta]. \quad (15)$$

$S_1(\vec{r}_a) \rightarrow 0$ for all values of θ_a . This condition guarantees that the behavior of the atomic wave function at the nucleus is not changed by the presence of the ion.

The second-order terms in Eq. (7) lead to

$$\xi \frac{\partial}{\partial r_a} S_2 = \frac{1}{2} [\nabla^2 S_1 - (\nabla S_1)^2] + \frac{(\nu - 1)}{r_a} \frac{\partial}{\partial r_a} S_1. \quad (10)$$

This differential equation can be solved by a tedious but straightforward calculation, using elliptic coordinates. The solution is

Note that we have dropped the subscript on θ since $\theta_a = \theta_b$.

In order to perform the surface integral in Eq. (14), we introduce the variable

$$y = \frac{1}{2} \xi R (\sec \theta - 1) = \xi (r_a - \frac{1}{2} R). \quad (16)$$

The infinitesimal element of surface area becomes

$$ds = (\pi R / \xi) (1 + 2y / \xi R) dy. \quad (17)$$

Since $u(r_a)$ decreases rapidly as r_a is increased, the major contribution to the integral comes from the region around $y=0$. Retaining only those terms necessary for our desired level of accuracy, we can write

$$u_0(r_a) = u_0(R/2) [1 + (2/\xi R)(\nu - 1)y] \exp(-y), \quad (18a)$$

$$S_1 = (1/\xi) (\frac{1}{2} - \ln 2), \quad (18b)$$

$$S_2 = -3/4 \xi^3 R. \quad (18c)$$

With these approximations the surface integral becomes

$$- \int_{\mathfrak{M}} u(\vec{r}_a) \frac{\partial}{\partial n} u(\vec{r}_a) ds = \frac{\pi}{2} R \left(\frac{4}{e} \right)^\nu u_0^2 \left(\frac{R}{2} \right) \times \left(1 + \frac{\nu^2}{R} \left(\frac{3}{2} \nu - 1 \right) \right). \quad (19)$$

The denominator in Eq. (14) involves the integral of $u^2(r_a)$ over all space. It is straightforward to show that

$$\int u^2(\vec{r}_a) d\vec{r}_a = \int u_0^2(\vec{r}_a) d\vec{r}_a + O(1/\xi R)^2 \approx 1. \quad (20)$$

Hence our final expression for the energy difference is

$$\Delta E(R) = \pi R \left(\frac{4}{e} \right)^\nu u_0^2 \left(\frac{R}{2} \right) \left[1 + \frac{\nu^2}{R} \left(\frac{3}{2} \nu - 1 \right) + O \left(\frac{1}{R^2} \right) \right]. \quad (21)$$

This equation was derived in 1955 by Holstein⁶ for the special case of $\nu=1$. The first term has been given by Holstein⁴ for $\nu=1$, and by Smirnov^{7,8} for a general value of ν . We have calculated the second term in order to obtain one indication of the rate of convergence of this series development. For the alkali ions the coefficient of $1/R$ in this second term is between 3.5 and 6.3. Thus even for $R \approx 20$, this term is not negligible.

In applying Eq. (21) the constant ν can easily be obtained from the ionization energy of atom X . The only uncertainty is in the constant q , that is in the magnitude of the asymptotic wave function for the atom. Several methods are available for estimating this constant. We list here four possible techniques.

(a) The Hartree-Fock approximation gives a reasonable estimate of the valence-electron wave function at small and intermediate values of r . The constant q could therefore be estimated by fitting $u_0(r)$ to the Hartree-Fock solution at a suitable distance from the origin. This technique was recommended by Smirnov⁹; however, the result depends on the point at which the fit is made, and we do not know of a proper procedure for choosing this matching point. In most cases one should not use the Hartree-Fock wave function directly in the asymptotic region, since the incorrect energy associated with that approximation will lead to a considerable error in the wave function at large distances from the atom.

(b) At integral values of n , $u_0(r)$ has the same asymptotic form as the orbitals of the hydrogen atom. The normalization constant of those orbitals is known analytically, and can therefore be interpolated for nonintegral values of n . The resulting value, which we will call the Coulomb approximation, is

$$q = q_c \equiv (2\xi)^\nu / \nu^{1.5} \Gamma(\nu). \quad (22)$$

(c) Seaton¹³ has shown that an estimate of the normalization constant can be obtained from quantum defect theory. The quantum defect μ is the difference between the principal quantum number of an orbital, n , and the effective quantum number ν derived from the energy through Eq. (3). The normalization constant q can then be obtained from the Coulomb approximation value q_c using

$$q = q_c \left(1 - (2\epsilon)^{3/2} \frac{\partial \mu}{\partial \epsilon} \right)^{-1/2}, \quad (23)$$

where ϵ is the binding energy of the valence orbitals. From the observed valence energy levels one can deduce the value of μ at several values of ϵ and thus can estimate the derivative $\partial \mu / \partial \epsilon$. However, for atoms in which the ground state is well separated from the excited states, the accuracy

with which one can obtain this derivative is uncertain.

(d) The behavior of a valence electron outside the core can be simulated very well through the use of a model potential¹⁴ or pseudopotential.¹⁵ By integrating the Schrödinger equation with such a potential and normalizing the resulting eigenfunction, the appropriate value of q can be derived. Unlike the previous techniques, this method requires the use of a computer, but it is the method which we recommend when suitable potentials are available.

III. COMPARISON WITH VARIATIONAL CALCULATIONS

The simplest test of the theory of Sec. II is by application to the interaction of H^+ with H . Here the atomic wave function $u_0(r)$ is known exactly, and very accurate calculations of the interaction are available. A comparison of the predictions of Eq. (21) with the exact calculations¹⁶⁻¹⁸ is given in Table I. It can be seen that the error decreases from about 20% at a separation of 4 bohrs to 2% at 14 bohrs. The region with greatest influence upon thermal collisions is around 12-15 bohrs, and at such separations Eq. (21) gives very good results.

Let us now examine the alkali atoms for which the undistorted valence orbitals $u_0(r)$ are not known exactly. The normalization constant q has been calculated by the four techniques described in Sec. II and the results are shown in Table II. The Hartree-Fock fit is taken directly from Smirnov.⁸ In applying the quantum defect method we have made a quadratic fit to $\mu(\epsilon)$. The model potential wave functions were kindly supplied by Norcross.¹⁴ The pseudopotentials used to generate the results in the final column will be described below.

The values of q derived from the model potential and pseudopotential eigenfunctions are significantly higher than the Coulomb approximation. The sense of this correction is predicted by the quantum defect theory, but the magnitude of the correction is underestimated for the heavier alkalis. The Hartree-Fock fits of Smirnov give re-

TABLE I. Comparison of exact and approximate energy splittings in H_2^+ .

R	Approx.	Exact
4	1.213×10^{-1}	1.005×10^{-1}
6	2.371×10^{-2}	2.132×10^{-2}
8	4.196×10^{-3}	3.964×10^{-3}
10	7.015×10^{-4}	6.776×10^{-4}
12	1.130×10^{-4}	1.104×10^{-4}
14	1.774×10^{-5}	1.745×10^{-5}
16	2.732×10^{-6}	2.698×10^{-6}

TABLE II. Calculations of the normalization constant q for the alkali-atom ground states.

Atom	Hartree-Fock	Coulomb approx.	Quantum defect	Model potential	Pseudopotential
Li	0.765	0.807	0.813	0.814	0.814
Na	0.75	0.752	0.764	0.768	0.767
K	0.535	0.570	0.589	0.600	0.598
Rb	0.49	0.532	0.555	0.572	0.568
Cs	0.41	0.467	0.491	0.514	0.509

sults which appear to be inferior to the Coulomb approximation.

Having obtained q , we can substitute $u_0(r)$ into Eq. (21) and evaluate the energy splittings in the interaction between the positive ions and neutral alkali atoms. Unfortunately there are no exact results for comparison. However, we can compare with the results of model potential and pseudopotential calculations. For Li_2^+ , Na_2^+ , Rb_2^+ and Cs_2^+ we have computed the lowest two potential-energy curves by the pseudopotential approach. The valence electron is considered to interact with both atomic cores through a potential

$$V(r) = \sum_i V_i(r) \mathcal{P}_i, \quad (24a)$$

where

$$|V_i(r) = A_i \exp(-\xi_i r^2) - \frac{\alpha_d}{2(r^2 + d^2)^2} - \frac{\alpha_q}{2(r^2 + d^2)^3} - \frac{1}{r}, \quad (24b)$$

and \mathcal{P}_i is the angular-momentum projection operator. A tabulation of the potential parameters together with a description of the pseudopotential method can be found in the review by Bardsley.¹⁵ The valence energy of the molecular ion in each of the two states was computed by a variational calculation with a trial wave function made up a linear combination of twelve atomic orbitals, six upon each atom. These orbitals were taken to be Slater orbitals

$$\phi(r) \propto r^n e^{-br}.$$

Following standard practice, integral values were

TABLE III. Energy splittings between the lowest ${}^2\Sigma_g$ and ${}^2\Sigma_u$ states of Li_2^+ .

R	$\Delta E(R)$			
	A	B	C	D
6	0.1340	0.1090	0.1079	0.1079
8	0.0764	0.0648	0.0641	0.0642
10	0.0365	0.0336	...	0.0331
12	0.0156	0.0155	0.0155	0.0153
14	0.0063	0.0065
16	0.0024	0.0025	0.0024	...

used for n , and the orbital exponents were varied in order to minimize the energy.

In Table III, the energy splitting between the lowest ${}^2\Sigma_g$ and ${}^2\Sigma_u$ states is presented as a function of nuclear separation. We have applied Eq. (21) using the values of q derived from the atomic wave functions supplied by Norcross to obtain the results shown in the column A. Column B contains the results of our variational calculations using the pseudopotential, and columns C and D give the results of variational calculations using model potentials by Dalgarno, Bottcher, and Victor,¹⁹ and by McMillan,²⁰ respectively. Distances and energies are given in atomic units.

The results of our JWKB calculation are considerably higher than the variational calculations at $R=6$, but at larger separations the two methods give compatible results. This behavior is consistent with that found in H_2^+ .

In Table IV the results for Na^+ -Na are shown and the trends are similar to those seen in Li^+ -Li. Columns A and B contain the results of our JWKB and pseudopotential calculations, and column C gives the model potential results of Bottcher, Allison and Dalgarno.²¹ Column D shows the results of *ab initio* calculations, using the Hartree-Fock method, by Bertoncini and Wahl.²²

In Table V the JWKB predictions for Rb_2^+ and Cs_2^+ , again shown in the columns marked A, are compared with the pseudopotential variational calculations, which are in columns B. The comparison extends to larger values of the internuclear distance. Once again the difference in the two results decreases as R is increased from 8 to 16 or 20 but at larger values of R the results diverge

TABLE IV. ${}^2\Sigma_g$ - ${}^2\Sigma_u$ energy splittings in Na_2^+ .

R	$\Delta E(R)$			
	A	B	C	D
6	0.1374	0.1018	0.0976	0.0994
8	0.0843	0.0650	0.0623	0.0667
10	0.0425	0.0359	...	0.0381
12	0.0191	0.0177	0.0171	...
14	0.0080	0.0079
15	0.0051	0.0047
16	0.0032	0.0032	0.0032	...

TABLE V. ${}^2\Sigma_g^- - {}^2\Sigma_u$ energy splittings in Rb_2^+ and Cs_2^+ .

R	$\Delta E(R)$			
	Rb_2^+		Cs_2^+	
	A	B	A	B
8	1.1×10^{-1}	7.2×10^{-2}	1.1×10^{-1}	7.7×10^{-2}
12	4.0×10^{-2}	3.3×10^{-2}	5.0×10^{-2}	3.8×10^{-2}
16	9.9×10^{-3}	9.6×10^{-3}	1.4×10^{-2}	1.3×10^{-2}
20	2.0×10^{-3}	1.9×10^{-3}	3.2×10^{-3}	3.1×10^{-3}
24	3.5×10^{-4}	3.0×10^{-4}	6.2×10^{-4}	5.5×10^{-4}
28	5.8×10^{-5}	4.5×10^{-5}	1.1×10^{-4}	9.0×10^{-5}

again. For $R > 20$ we constrained the orbital exponents appearing in the trial wave functions in our variational calculations, in order to minimize numerical errors and to fit, as well as possible, the proper asymptotic form for the atomic wave functions.

The over-all pattern of these results is clear. At moderate values of the nuclear separation the JWKB result overestimates the energy splitting. For such values the term of order $1/R$ in Eq. (21) is significant and it is unreasonable to expect the higher-order terms to be negligible. At values of R such that $\Delta E(R)$ is between 10^{-3} and 10^{-2} the JWKB and variational methods give results that are in close agreement. For larger values of R we believe that the JWKB results should be more reliable.

IV. SYSTEMS WITH THREE VALENCE ELECTRONS

We now consider systems such as $\text{He}^+ - \text{He}$ in which the neutral atom has two valence electrons. In this situation one must examine the effects of the electron spin and the Pauli principle.

Let us assume that the single valence electron in the ion can be represented by an orbital $\chi(r)$. For the neutral atom we are mostly concerned with the form of the wave function when one electron is far removed from the nucleus. Let us suppose that this electron is in an orbital $\phi_0(r)$. The second valence electron will behave very much as if it were in a positive ion and can be described by the orbital $\chi(r)$. Thus as $r_1 \rightarrow \infty$ the two valence electrons can be described by a wave function

$$\psi_0(r_1, r_2) = N \phi_0(r_1) \chi(r_2) (\alpha_1 \beta_2 - \beta_1 \alpha_2) / \sqrt{2} \quad (25)$$

in which α and β denote the two spin states for the electrons and N is a normalization constant. We assume that the single-particle orbitals are normalized.

At large values of the internuclear distance the wave function for the three valence electrons in the ion-atom pair can be approximated by

$$\Psi^\pm(\vec{r}_1, \vec{r}_2, \vec{r}_3) \approx (1/\sqrt{3})(1 + \mathbf{e} + \mathbf{e}^2) [\psi_0(r_{1a}, r_{2a}) \chi(r_{3b}) \alpha_3 \pm \psi_0(r_{1b}, r_{2b}) \chi(r_{3a}) \alpha_3] \quad (26)$$

in which \mathbf{e} is the operator describing the cyclic permutation of electron coordinates 1, 2, and 3. The major effect of the distortion of the two particles will be seen in the more diffuse orbital of the neutral atom $\phi_0(r)$. The change in this orbital can be studied by the method used in Sec. II. We therefore replace $\phi_0(r)$ by $\phi(r)$ which can be expanded in the manner used for $u(r)$ earlier.

Again our aim is to compute the difference in the energies of the two molecular states Ψ^+ and Ψ^- , and this can be accomplished using Green's theorem. There are at least three ways in which this theorem can be applied. For example in Eq. (12) the region \mathcal{L} can be defined as that portion of configuration space in which at least two of the valence electrons are closer to nucleus A than to nucleus B. The corresponding hypersurface \mathcal{N} is such that one electron is on the median plane and the remaining two valence electrons are on opposite sides of that plane.

Let us now assume that the nuclear separation is sufficiently large that the function $\chi(r)$ is negligible for $r > R/2$, and that only the diffuse orbital $\phi(r)$ extends up to and over the median plane. The theory described in Sec. II can then be repeated; the only major differences arise from the presence of the spin functions and permutation operators. If the wave function for the neutral atom is expressed in the form (25), we obtain

$$\Delta E(R) \approx -N^2 \pi R (4/e)^{\nu} \phi_0^2(R/2) f(\nu, R) \quad (27)$$

with

$$f(\nu, R) = 1 + (\nu^2/R)(\frac{3}{2}\nu - 1), \quad (28)$$

in which ν is defined by Eq. (3) in terms of the ionization potential of the neutral atom. Equation (27) can be rewritten in terms of the electron density $\rho(r)$ in the neutral atom

$$\Delta E(R) \approx -(\pi R/2)(4/e)^{\nu} \rho(R/2) f(\nu, R). \quad (29)$$

Expressed in this way it appears that the effect of the spin and the Pauli principle is to change the sign of the energy splitting and reduce its magnitude by a factor of 2. This has been pointed out by Smirnov and collaborators.⁷⁻⁹ This factor arises because in order to transfer from one atom to the other the electron which is close to the median plane must have the appropriate spin direction to be accepted by the ion. The probability for this is $\frac{1}{2}$.

We must now examine the asymptotic form of the electron density in the He atom. We can expand $\phi_0(r)$ as in Eq. (2) and obtain

$$\rho(r) = 2N^2 \phi_0^2(r) \approx 2N^2 (q^2/4\pi) r^{2\nu-2} e^{-2\xi r}. \quad (30)$$

The only remaining problem is to determine the product Nq . In the early work of Smirnov^{7,8} there

seems to be the implication that the asymptotic electron density is equal to that of a single-valence atom of the same ionization potential. On the other hand the Hartree-Fock approximation would suggest that the electron density in He is twice that amount since each electron can be found in the asymptotic region and the electrons move independently. We would expect that this latter result is more nearly correct, but that the effects of radial correlation should cause the factor of comparison to be slightly less than 2. The later papers by Smirnov and his colleagues¹⁰⁻¹² support this view. Unfortunately the earlier version of Smirnov's work seems to have been followed by Johnson²³ in his work on Ar⁺-Ar interactions.

We have examined the wave functions computed for the He atom by Kinoshita,²⁴ by Hart and Herzberg,²⁵ and by Winkler and Porter.²⁶ Although these are extensive variational calculations, the trial wave functions do not have the appropriate asymptotic form. Nevertheless, by examining the wave functions for $r_1=0$ and $r_2 \approx 5$ we are able to estimate that the appropriate value of Nq lies between 2.7 and 2.9, which is slightly smaller than the Hartree-Fock value.

In Table VI we present the splittings calculated with the value of Nq equal to 2.84, and compare the results with the variational calculations of Matsen and colleagues^{27, 28} using a large trial wave function and those of Moiseiwitsch with a very simple trial function.²⁹ All three results are in fair agreement, and this again gives us confidence that we can extrapolate our results to higher values of r .

Duman¹¹ has studied many systems which have the same valence structure as He₂⁺, namely Be₂⁺, Mg₂⁺, Ca₂⁺, Sr₂⁺, Ba₂⁺, Zn₂⁺, Cd₂⁺, and Hg₂⁺. He obtained estimates of the product Nq by fitting to Hartree-Fock wave functions. His expressions for $\Delta E(R)$ have the correct asymptotic form but may be in error by up to 50%, due to the uncertainty in the value of Nq and the inclusion of only a single term in the expansion of $\Delta E(R)$. The corresponding error in the computed cross sections should only be about 10%.

TABLE VI. Energy splittings between the $^2\Sigma_u$ and $^2\Sigma_g$ states of He₂⁺.

R	$\Delta E(R)$		
	This work	Matsen <i>et al.</i>	Moiseiwitsch
4	3.8×10^{-2}	3.4×10^{-2}	3.4×10^{-2}
5	10.9×10^{-3}	9.9×10^{-3}	10.4×10^{-3}
6	3.1×10^{-3}	2.8×10^{-3}	3.1×10^{-3}
7	8.5×10^{-4}	...	8.9×10^{-4}
8	2.4×10^{-4}	...	2.5×10^{-4}
9	6.5×10^{-5}	...	6.6×10^{-5}
10	1.8×10^{-5}	...	1.6×10^{-5}

V. TRANSFER OF ELECTRONS WITH NONZERO ANGULAR MOMENTUM

In our previous discussions we assumed that the valence electron which is transferred was in an s orbital. Let us now relax that assumption, and replace the factor $1/\sqrt{4\pi}$ in the undistorted wave function $u_0(r)$, as in Eq. (2), by a general spherical harmonic $Y_l^m(\Omega)$. Note that coefficients in the series expansion of $u_0(r)$ are changed; for example we find

$$p = \frac{1}{2}\nu[l(l+1) - \nu(\nu-1)].$$

Examination of our previous analysis shows that we need to know the wave function for the valence electron only on the median plane close to the midpoint between the nuclei. This is also true in the general case, and so we can assume that the polar angles θ_a and θ_b are small. We can therefore approximate the spherical harmonic $Y_l^m(\theta, \phi)$ by

$$Y_l^m(\theta, \phi) \approx e^{im\phi} \left(\frac{(2l+1)}{4\pi} \frac{(l+m)!}{(l-m)!} \right)^{1/2} \frac{\sin^m \theta}{2^m m!} \times \left(1 - \frac{(l+m+1)(l-m)}{2(m+1)} \frac{\theta^2}{2} \right). \quad (31)$$

This expression can be obtained using the generating functions for the Gegenbauer polynomials.³⁰

The first effect of the angular dependence of $u_0(\vec{r})$ occurs in Eq. (7), since ∇u_0 now has a component perpendicular to \vec{r}_a . In the evaluation of S_1 , this component may be neglected, even though $(1/u_0) \times (\partial u_0 / \partial \theta_a)$ becomes infinite as $\theta_a \rightarrow 0$ when $m \neq 0$, since $\partial \nu / \partial \theta_a$ is very small. The angular derivatives do contribute to S_2 and Eq. (10) becomes

$$\xi \frac{\partial}{\partial r_a} S_2 = \frac{1}{2} \left[\frac{1}{r_a} \frac{\partial^2}{\partial r_a^2} (r_a S_1) - \left(\frac{\partial S_1}{\partial r_a} \right)^2 \right] + \frac{(\nu-1)}{r_a} \frac{\partial}{\partial r_a} S_1 + \frac{1}{r_a^2} \frac{1}{u_0} \frac{\partial u_0}{\partial \theta_a} \frac{\partial S_1}{\partial \theta_a} \quad (32)$$

in which S_1 is given by Eq. (9). Using Eq. (31) in the evaluation of $\partial u_0 / \partial \theta_a$ we obtain an additional contribution to S_2 of $\nu^2 m / 2R$.

The second effect is that the normal derivative on the medium plane contains a term involving the angular derivative

$$\begin{aligned} \frac{\partial}{\partial n} u(\vec{r}_a) &= \left(\cos \theta_a \frac{\partial}{\partial r_a} - \frac{1}{r_a} \sin \theta_a \frac{\partial}{\partial \theta_a} \right) u(\vec{r}_a) \\ &\approx -\cos \theta_a u(\vec{r}_a) \left[\xi \left(1 - \frac{1}{\xi^2 R} \right) + \frac{2}{R} (m - \nu + 1) \cos \theta_a \right]. \quad (33) \end{aligned}$$

Finally the spherical harmonics must be included in Eq. (18a). For $m > 0$ the function $u_0(\vec{r}_a)$ will vanish at the midpoint between the nuclei, and hence

we expect the energy splitting to be reduced significantly.

Retaining the first two terms in powers of $1/R$, we obtain

$$\Delta E(R) = \frac{(2l+1)}{4(m!)} \frac{(l+m)!}{(l-m)!} \left(\frac{\nu}{2R}\right)^m R \bar{u}_0^2 \left(\frac{R}{2}\right) \left(\frac{4}{e}\right)^\nu \times \left(1 + \frac{\nu}{2R} [\nu(3\nu-2) + m(2\nu-3m-3) - 2(l+m+1)(l-m)]\right) \quad (34)$$

in which $\bar{u}_0(r)$ is the radial part of $u_0(\vec{r})$, i.e.,

$$u_0(\vec{r}) = \bar{u}_0(r) Y_l^m(\Omega). \quad (35)$$

The leading term in this expression was first derived by Smirnov.⁸ For H_2^+ the asymptotic expansion can be obtained by alternative means,^{17,18} and our results agree with the first two terms in that expansion for those states with $m=l=\nu-1$. For the other states of H_2^+ the additional degeneracies which occur among the excited states of H lead to different expressions for the molecular splittings, which are not applicable to other ions.

For states with odd values of m the symmetry operations of reflection in the median plane and inversion do not give the same result. The molecular state ψ_+ is ungerade, and ψ_- is gerade, and thus in molecules such as B_2^+ and Al_2^+ the ${}^2\Pi_g$ state lies above the ${}^2\Pi_u$ state.

Let us next examine the rare-gas systems Ne_2^+ , Ar_2^+ , Kr_2^+ , and Xe_2^+ in which the atomic ion has a single vacancy in the outer p shell. Just as in the case of He we find that the levels are reversed relative to systems with a single valence electron. Thus the ${}^2\Sigma_g$ and ${}^2\Pi_u$ states lie above the ${}^2\Sigma_u$ and ${}^2\Pi_g$ states, respectively. Once again, if the electrons are considered to move independently, the magnitude of the $g-u$ splittings would be equal to that of a system with a single valence electron with the same ionization potential, but correlation effects should reduce the splittings slightly.

Cohen and Schneider³¹ have recently reported variational calculations of the lowest four states of Ne_2^+ . In Table VII their results for the $g-u$ splittings between the ${}^2\Sigma$ states and the two ${}^2\Pi$ states

are compared to the predictions of Eq. (34). We have used Hartree-Fock functions for $\bar{u}_0(r)$, taken from the tabulation by Froese-Fischer.³² There should be two errors associated with the use of such functions. Firstly the Hartree-Fock approximation overestimates the electron binding energy and thus $u_0(r)$ will fall off too rapidly as r is increased. Secondly correlation effects should lead to a slight reduction in the magnitude of the wave function in the asymptotic region. In these circumstances the good agreement that is found in Table VII may be a little misleading, and the correct values of the splittings may be slightly smaller. In order to extrapolate to much larger values of R , one should use the proper asymptotic form. Unfortunately we do not have an accurate estimate of the appropriate constants Nq to use for this system.

Johnson²³ has applied the JWKB approach to Ar_2^+ , following the work of Smirnov, keeping only the leading term in the expansion in $1/R$. His result is consistent with Eq. (34) except for the presence of the factor $\frac{1}{2}$ which was introduced by Smirnov to allow for spin effects and which we believe to be spurious. Johnson used the Hartree-Fock orbitals in estimating the asymptotic constants Nq , and the values so obtained may be slightly too high. Overall we estimate that the energy differences obtained by Johnson may be too small at large distances, although at smaller distances the neglect of the second term in Eq. (34) may partially compensate for the spurious factor of $\frac{1}{2}$.

In studying the long-range interactions of systems in which the neutral atom or ion has nonzero angular momentum and nonzero spin, one should consider the effects of the spin-orbit interaction. At the large values of R which are of critical importance in low-energy collisions, it is reasonable to assume that this interaction is independent of R . The effect of the spin-orbit interaction at $R=\infty$ is known empirically, and the complete Hamiltonian can then be diagonalized at all large values of R . This method has been followed by Duman and Smirnov,¹² Johnson,²³ and by Cohen and Schneider.³¹

TABLE VII. Gerade-ungerade energy splittings in Ne_2^+ .

R	Cohen and Schneider		This work	
	Σ	Π	Σ	Π
4	7.1×10^{-2}	1.4×10^{-2}	7.1×10^{-2}	1.4×10^{-2}
5	2.1×10^{-2}	3.4×10^{-3}	2.2×10^{-2}	3.4×10^{-3}
6	6.2×10^{-3}	8.7×10^{-4}	6.5×10^{-3}	8.4×10^{-4}
7	1.8×10^{-3}	2.4×10^{-4}	1.9×10^{-3}	2.1×10^{-4}
8	5.2×10^{-4}	5.0×10^{-5}	5.5×10^{-4}	5.3×10^{-5}

VI. SUMMARY AND CONCLUSIONS

We have followed through the JWKB method for computing the gerade-ungerade energy splittings in homonuclear molecular ions, retaining two terms in the expansion in inverse powers of the nuclear separation, and have performed variational calculations in order to check the JWKB method. At those separations for which the splittings are between 10^{-3} and 10^{-2} a.u., the two methods

give compatible results. At smaller separations the second term in the expansion gives a significant contribution, and the comparison with the variational calculations suggests that the higher-order terms are not negligible. At larger separations the variational method involves difficult numerical problems, and the JWKB method may lead to better results.

Several authors have used different forms for $\Delta E(R)$ in studies of symmetric charge exchange. Rapp and Francis⁵ performed a simple LCAO calculation with scaled hydrogenic 1s orbitals and obtained

$$\Delta E(R) \approx (1/\nu^2)R \exp(-R/\nu), \quad (36)$$

again with ν equal to $(2\epsilon)^{-1/2}$. This expression has the proper exponential factor but the power of R multiplying that factor is correct only if $2\nu = m + 2$. The variational calculation by Moiseiwitsch²⁷ on He_2^+ and by McConnell and Moiseiwitsch³³ on Hg_2^+ lead to the same form but with a different pre-exponential constant. For these systems the resulting error in $\Delta E(R)$ does not lead to serious errors in the computed cross sections for charge exchange. However, for the alkali-metal atoms the error is more serious. For example in Cs^+ -Cs collisions at thermal energy the critical region is $R \approx 35a_0$. At such separations the value of $\Delta E(R)$ given by Eq. (36) is approximately 70 times smaller than the prediction of our analysis. This would lead to a significant underestimation of the charge-exchange cross section.

Dewangan³⁴ has recently suggested that within the two-state impact-parameter approximation there is an exact scaling law by which the cross sections for all symmetric charge transfer reactions can be related to the corresponding cross sections in H^+ -H collisions. The scaling law is based upon a calculation of the molecular energy splittings by the simple LCAO method using hydrogenic 1s orbitals. As we have seen above, this method gives an incorrect asymptotic form, and the scaling law cannot be derived using the proper expression for $\Delta E(R)$.

The one-electron model upon which we have based our calculation is directly applicable to those systems in which either the neutral atom or ion has a ground state with 1S symmetry. Most of the systems of major physical interest are in this category. For other cases, such as O^+ -O and Fe^+ -Fe, one must examine more carefully the coupling of the outermost electron with the remaining electrons. Although these problems have been discussed briefly by Duman and Smirnov,^{8,12} we believe that further work is necessary.

According to this theory the long-range behavior of the energy splitting can be expressed in the form

$$\Delta E(R) = AR^{2\nu-1-m} \exp\left(-\frac{R}{\nu}\right) \left[1 + \frac{B}{R} + O\left(\frac{1}{R^2}\right)\right]. \quad (37)$$

The parameters ν and B are determined from the atomic ionization potential, and m is the component of the orbital angular momentum along the internuclear axis. In order to calculate the constant A , one needs to know the magnitude of the electron density of the neutral atom in the asymptotic region. Unfortunately, most of the published atomic wave functions do not have the proper asymptotic form, and so accurate values cannot yet be given for this constant. Although the asymptotic region contributes little to the energy of an atom, it is clearly of great interest in regard to the interaction of the atom with neighboring particles, and it is to be hoped that more attention will be given to this region in future calculations of wave functions.

In future papers we plan to apply this theory in the calculation of charge transfer cross sections for both positive and negative ions.

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