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Technical Report

**Asymptotically Exact Calculation  
of the Exchange Energies  
of One-Active-Electron Diatomic Ions  
with the Surface Integral Method**

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## Abstract

We present a general procedure, based on the Holstein-Herring method, for calculating exactly the leading term in the exponentially small exchange energy splitting between two asymptotically degenerate states of a diatomic molecule or molecular ion. The general formulas we have derived are shown to reduce correctly to the previously known exact results for the specific cases of the lowest  $\Sigma$  and  $\Pi$  states of  $\text{H}_2^+$ . We then apply our general formulas to calculate the exchange energy splittings between the lowest states of the diatomic alkali cations  $\text{K}_2^+$ ,  $\text{Rb}_2^+$ , and  $\text{Cs}_2^+$ , which are isovalent to  $\text{H}_2^+$ . Our results are found to be in very good agreement with the best available experimental data and *ab initio* calculations.

## 1 Introduction

The exchange energy splitting  $\Delta E$  between asymptotically degenerate electronic states of molecules is very difficult to calculate accurately by conventional variational methods, since it vanishes exponentially with the internuclear distance  $R$  and consequently can easily be much smaller than the errors caused by the use of a finite basis set. Yet, the accurate calculation of exchange energy splittings is of great importance in the theories of molecular binding and of magnetism. The exchange energy splittings also play a crucial role in charge exchange processes in stellar and atmospheric physics. For example, the exchange effects in molecules such as oxygen  $\text{O}_2$ , nitrogen  $\text{N}_2$ , and ozone  $\text{O}_3$  are of interest in a number of processes [1]. Recently, investigations of photo-association of cold alkali atoms have required accurate benchmark values for the exchange energies of these diatomic systems [2].

In 1952 Holstein [3, (a)] showed that in the case of the hydrogenic molecular cation  $\text{H}_2^+$ , the exchange energy splitting  $\Delta E = \hbar\omega$ , where  $\omega$  is the frequency of tunneling between the two symmetric potential wells, could be calculated from the current flowing across the mid-plane  $\mathcal{M}$  between the two identical nuclei  $A$  and  $B$ . If  $\Psi_g$  and  $\Psi_u$  are respectively the *gerade* and *ungerade* electronic wavefunctions, then

$$\Delta E = -2 \frac{\int_{\mathcal{M}} \Psi_A \nabla \Psi_A \cdot d\mathbf{S}}{1 - 2 \int_{\text{right}} \Psi_A^2 dV}, \quad (1)$$

where  $\Psi_A = (\Psi_g + \Psi_u)/\sqrt{2}$  is the localized atomic-like wave function concentrated near nucleus  $A$ ,  $d\mathbf{S}$  is a differential surface element of the mid-plane  $\mathcal{M}$ , and the integral in the denominator is a volume integration over the half-space containing nucleus  $B$ . Herring argued that the localized function  $\Psi_A$  could be replaced by an approximation  $\chi_A$ , i.e. the solution of the  $\text{H}_2^+$  problem in a space that excludes a small sphere centered on nucleus  $B$  [3, (c)]. This function  $\chi_A$  could be written as the product of the (unperturbed) ground state wave function  $\psi_0(r_1)$  of the hydrogen atom and a function  $g_A(r_1)$ , where  $r_1$  is the distance between the electron and nucleus  $A$ . This is often designated as the Herring function and hence equation (1) is generally known as the Holstein-Herring (HH) formula.

The volume integral over the semi-infinite space on the right of the mid-plane  $\mathcal{M}$  in the denominator of eq. (1) decreases exponentially with  $R$  at the same rate as the numerator. In other words, if to leading order the numerator is of the order  $e^{-cR}$ , then the denominator has the form  $1 - O(e^{-cR})$ . Thus when the internuclear distance  $R$  is sufficiently large, the denominator can be taken as unity and the surface integral term in the numerator is a good asymptotic approximation to the exchange energy splitting.

The Holstein-Herring method had limited applications until in 1990 Tang, Toennies, and Yiu [4, (a)]

showed that in the Holstein-Herring formula one could replace the exact localized wave function  $\Psi_A$  with the solution of the unsymmetrized Rayleigh-Schrödinger perturbative equation to calculate the leading terms in the ground-state exchange energy splitting of  $\text{H}_2^+$ . Specifically, Tang, Toennies and Yiu [4, (b)] used the leading terms of an expansion in powers of  $R^{-1}$  of the polarization wave function  $\Phi_A(\lambda)$  obtained by solving the perturbation equation

$$\left[ \left( -\frac{1}{2} \nabla^2 - \frac{1}{r_A} \right) + \lambda \left( \frac{1}{R} - \frac{1}{r_B} \right) \right] \Phi_A(\lambda) = \epsilon_A(\lambda) \Phi_A(\lambda),$$

where  $\lambda$  is an ordering parameter which equals unity for  $\text{H}_2^+$ . Expanding  $\epsilon_A$  and  $\Phi_A$  as Taylor series in powers of  $\lambda$  about  $\lambda = 0$  yields

$$\begin{aligned} \epsilon_A^p(\lambda) &= \sum_{i=0}^{\infty} \frac{1}{i!} \left. \frac{\partial^i \epsilon_A(\lambda)}{\partial \lambda^i} \right|_{\lambda=0} \lambda^i \\ \Phi_A^p(\lambda) &= \sum_{i=0}^{\infty} \frac{1}{i!} \left. \frac{\partial^i \Phi_A(\lambda)}{\partial \lambda^i} \right|_{\lambda=0} \lambda^i \end{aligned}$$

Insertion of these expansions truncated at order  $\lambda^N$  into the surface term of the Holstein-Herring (HH) formula (1) indeed yields the desired coefficients  $a_i$  of (2) in the limit  $N \rightarrow \infty$ , although for any finite  $R$  the polarization expansion converges as  $N \rightarrow \infty$  to a symmetric function for which the integrand in the Holstein-Herring formula is identically zero! The paradoxical convergence properties of this procedure were subsequently elucidated by Scott, Babb, Dalgarno, and Morgan [5–7], who proved that  $\Psi_A$  can be a “polarized” wave function, i.e. an atomic wave function localized at a particular nucleus but perturbed by the other nuclear center, and consequently without either gerade or ungerade symmetry, but (1) could nonetheless be used to generate the correct asymptotic series expansions for the exchange energies. Thanks to the work of Morgan and Simon [8], we know that the true localized wave function  $\Psi_A = (\Psi_g + \Psi_u)/\sqrt{2}$  has an asymptotic expansion  $\Phi_A^{1/R}$  in powers of  $R^{-1}$  about atom  $A$ , which is *distinct* from the infinite polarization expansion  $\Phi_A^p$  of the wave function, and has very different convergence properties: whereas the  $1/R$  expansion is asymptotic and in general divergent for any finite  $R$ , the polarization expansion is usually convergent for sufficiently small  $\lambda$ , and for simple enough systems it may converge for finite  $R$  even for  $\lambda = 1$ . With this understanding and the realization that these findings involved a general underlying property [5], it was realized that the Holstein-Herring method was applicable to many-electron systems.

The subsequent developments of this procedure for estimating exchange energies by Tang and Toennies and their co-workers, and their numerical calculations of exchange energy splittings for several diatomic and triatomic molecules and molecular ions (see for example the most recent work in [4, (e)] and references therein), illustrate the need for more general analytical solutions and careful numerical analysis. The exchange energy splitting has an asymptotic series expansion, which can be written in the general form:

$$\Delta E = e^{-cR} R^b \left[ a_0 + \frac{a_1}{R} + \frac{a_2}{R^2} + \dots \right] + O(e^{-dR}), \quad (2)$$

where the exponential parameters  $c$  and  $d$  are state-dependent positive numbers related to the ionization potentials with  $c < d$ , the power  $b$  is a state-dependent real number, and the  $a_i$  are state-dependent real coefficients. In such a situation, assuming that  $c$  and  $b$  are accurately known, it is vital to determine the leading coefficient  $a_0$  as accurately as possible long before one needs to worry about the precise value of  $a_1$ , and the same applies to each  $i^{\text{th}}$  coefficient  $a_i$  in relation to  $a_{i+1}$ .

In principle, any bound state of a homonuclear diatomic molecule has a unique  $1/R$ -expansion which can be used to compute the exchange energy splitting between a pair of asymptotically degenerate molecular electronic states, but in practice complications can arise. The desired coefficients

$a_i$  cannot be obtained exactly in this way; rather, each coefficient is best represented as the sum of a sequence of rational numbers, and in general, this sequence is infinite. Thus the  $1/R$ -expansion can at best yield numerical approximations of these coefficients of greatly decreasing accuracy as  $i$  increases. This has been confirmed with computer algebra in the case of  $\text{H}_2^+$ . Convergence was found to be slow: even a  $1/R$ -expansion carried out to hundreds of terms, yielding a good value of  $a_0$ , yielded at best a moderately good approximation for  $a_1$  and a hopelessly inaccurate value for  $a_2$ . This can be readily demonstrated by an application of computer algebra on the known  $1/R$  expansion [8]. A method which can focus successively on the natural hierarchy of coefficients  $a_i$  is far more desirable. Thus, we aim for a formulation that gives the leading term as accurately as possible, subject to further refinement of the formulation for the higher-order coefficients.

The past results obtained for  $\text{H}_2^+$  can be generalized to more complicated diatomic systems. As a first generalization we consider a one-active-electron diatomic molecular ion, with a single electron shared by two identical nuclear charges, each surrounded by tightly bound core electrons, whose effect on the shared electron can be modeled using effective single-particle pseudopotentials. Thus, one has a singly-charged cation interacting with a neutral atom.

As a first step, we present a general formulation for this ion-atom case. Our present derivation is designed to identify carefully the pairwise exchange processes for more general situations, since this work is intended as the first of a series of articles on the calculation of exchange energies based on the Holstein-Herring method. In a future work, we shall present a straightforward generalization of this formulation to the *two-active* electron case. We will then be equipped to treat a number of cases including the 4-active electron case of  $\text{Ca}_2$ , which can be formally decomposed into combinations of 2-active electron formulations.

The analytical solutions presented here involve accurate results expressed in terms of asymptotic expansions. These provide us with an accurate benchmark for numerical analysis. The mathematical details in the derivations of these solutions are shown in the work of [9] and we present the resulting solutions here. The results are then tested on a number of diatomic alkali cations  $\text{M}_2^+$  isovalent to  $\text{H}_2^+$ , in particular  $\text{K}_2^+$ ,  $\text{Rb}_2^+$ ,  $\text{Cs}_2^+$  and compared to those resulting from our recent *ab initio* calculations [10–12]. Concluding remarks are made at the end.

## 2 General Formulation for a Diatomic Molecular Ion with One Active Electron

### 2.1 Coordinate Systems

We have chosen the following definitions. Let the internuclear axis joining nuclei  $A$  and  $B$  coincide with the  $z$ -axis, with the origin of the coordinate system located at the midpoint between the nuclei. Then nucleus  $A$  has Cartesian coordinates  $(0, 0, -R/2)$ , nucleus  $B$  has Cartesian coordinates  $(0, 0, R/2)$ , the internuclear distance is given by  $\overline{AB} = R$ , and the electron has Cartesian coordinates  $e_1[x_1, y_1, z_1]$ . We assume that the electron 1 is in the neighborhood of atom  $A$  before exchange, i.e.  $(A, e) + B$  and is in the neighborhood of atom  $B$  after exchange, i.e.  $A + (B, e)$ . In the following notation, the primed index is always related to the situation “after exchange”. Let us define:

$$\begin{aligned} A\mathbf{e}_1 &= \mathbf{r}_1 && \text{before exchange} \\ B\mathbf{e}_1 &= \mathbf{r}'_1 && \text{after exchange} \end{aligned}$$

Besides the Cartesian coordinates  $x, y, z$ , we also use:

- Spherical coordinates:  $r, \theta, \phi$  ( $r \geq 0, 0 \leq \theta \leq \pi, 0 \leq \phi \leq 2\pi$ );
- Cylindrical coordinates:  $\rho, \phi, z$  and
- Prolate spheroidal coordinates:  $\xi, \eta, \phi$  ( $1 \leq \xi \leq \infty, -1 \leq \eta \leq 1$ )

$$\xi = \frac{1}{R}(r_1 + r'_1) \quad \eta = \frac{1}{R}(r_1 - r'_1) \quad (3)$$

where  $r_1$  and  $r'_1$  are greater than zero.

These four coordinate systems are related by the well-known formulas:

$$\begin{aligned} x &= r \sin \theta \cos \phi = \rho \cos \phi = \frac{R}{2} ((\xi^2 - 1)(1 - \eta^2))^{\frac{1}{2}} \cos \phi \\ y &= r \sin \theta \sin \phi = \rho \sin \phi = \frac{R}{2} ((\xi^2 - 1)(1 - \eta^2))^{\frac{1}{2}} \sin \phi \\ z &= r \cos \theta \end{aligned}$$

Thus, the squares of the linear coordinates obey

$$\rho^2 = x^2 + y^2 = r^2 \sin^2 \theta \quad r^2 = \rho^2 + z^2 \quad (4)$$

and we also have:

$$r_1^2 = \rho_1^2 + (z_1 + R/2)^2 \quad r'^2_1 = \rho_1^2 + (z_1 - R/2)^2 \quad (5)$$

where  $z_1$  is equal to the projection of  $O\mathbf{e}_1$  onto the  $z$ -axis. Consequently:

$$\frac{\partial r_1}{\partial z_1} = 2 \frac{\partial r_1}{\partial R} \quad \text{and} \quad \frac{\partial r'_1}{\partial z_1} = -2 \frac{\partial r'_1}{\partial R} \quad (6)$$

In the following, we consider the wave functions  $\Psi_I(1) = \Psi_I(\mathbf{r}_1)$  and  $\Psi_{II}(1) = \Psi_{II}(\mathbf{r}'_1)$ . For  $\mathbf{e}_1$  before exchange:

$$\cos \theta_1 = \frac{z_1 + R/2}{\left[ \rho_1^2 + \left( z_1 + \frac{R}{2} \right)^2 \right]^{\frac{1}{2}}}$$

For  $\mathbf{e}_1$  after exchange:

$$\cos \theta'_1 = \frac{z_1 - R/2}{\left[ \rho_1^2 + \left( z_1 - \frac{R}{2} \right)^2 \right]^{\frac{1}{2}}}$$

which gives:

$$\frac{\partial \cos \theta_1}{\partial z_1} = 2 \frac{\partial \cos \theta_1}{\partial R} \quad \text{and} \quad \frac{\partial \cos \theta'_1}{\partial z_1} = -2 \frac{\partial \cos \theta'_1}{\partial R} \quad (7)$$

We also have:

$$\begin{aligned} \cos \theta_1 &= \frac{z_1 + R/2}{r_1} & \sin \theta_1 &= \frac{\rho_1}{r_1}, \\ \cos \theta'_1 &= \frac{z_1 - R/2}{r'_1} & \sin \theta'_1 &= \frac{\rho_1}{r'_1}. \end{aligned} \quad (8)$$



## 2.2 Wave Functions

In the general case of *one-active-electron* systems, such as diatomic alkali cations  $M_2^+$  isovalent to  $H_2^+$ , the atomic wave functions are expressed as linear combinations of unperturbed Slater-type functions  $\phi_A$  and  $\phi'_B$ . They are corrected by a polarization term  $\chi(\mathbf{r})$  and are written as:

$$\begin{aligned}\Psi_I(1) &= \chi_1(\mathbf{r}) \sum_A \phi_A(1) P_{\ell_A}^{m_A}(\cos \theta_1) \exp(im_A \phi_1), \\ \Psi_{II}(1) &= \chi_2(\mathbf{r}) \sum_B \phi'_B(1) P_{\ell'_B}^{m'_B}(\cos \theta'_1) \exp(im'_B \phi'_1),\end{aligned}\quad (9)$$

with

$$\begin{aligned}\phi_A(1) &= \mathcal{A}_A r_1^{\gamma_A} \exp(-\alpha_A r_1) \\ \phi'_B(1) &= \mathcal{B}_B r_1^{\delta'_B} \exp(-\beta'_B r_1)\end{aligned}$$

where  $\{\ell_A, m_A\}$  and  $\{\ell'_B, m'_B\}$  are the usual atomic quantum numbers, and  $\{\mathcal{A}_A, \gamma_A, \alpha_A\}$  and  $\{\mathcal{B}_B, \delta'_B, \beta'_B\}$  are known parameters characterizing the radial parts of the atomic wave functions. They can be derived from the solution of the *one-active-electron* Schrödinger wave equation for the atom under consideration.

The correction functions  $\chi_1$  and  $\chi_2$  introduced by Chibisov and Janev are given by equations (2.24) and (2.28) of their article [13]. In the limit where the internuclear distance  $R$  becomes very large, the following forms are used:

$$\begin{aligned}\chi_1 &= \left(\frac{R}{Z_2}\right)^{g_2} \exp[-g_2(\frac{Z_1}{R})] \\ \chi_2 &= \left(\frac{R}{Z_1}\right)^{g_1} \exp[-g_1(\frac{Z_2}{R})]\end{aligned}\quad (10)$$

where  $Z_1$  is the length of the projection of  $Ae$  onto the  $z$ -axis and  $Z_2$  is the length of the projection of  $Be$  onto the  $z$ -axis, and hence  $R = Z_1 + Z_2$ . Also  $g_1 = 1/\alpha_A$  and  $g_2 = 1/\beta'_B$ . These are the expressions of the functions  $\chi_1$  and  $\chi_2$  given by Chibisov and Janev in equation (2.62) of their work [13]. In the case of  $g_1 = g_2 = 1$  (i.e.  $\alpha_A = \beta'_B = 1$ ), the above corresponds to the large  $R$  limit of the Herring function for  $H_2^+$  [3, (c), eq. (23)].

Note that for hydrogenic systems, we have the inequalities:

$$\gamma_i \geq \ell_i \geq m_i \quad \delta'_i \geq \ell'_i \geq m_i$$

We further assume that the angles  $\phi_i$  remained unchanged:  $\phi_i = \phi'_i$  where  $i = 1, 2$ , so that<sup>1</sup>:

$$\begin{aligned}\Psi_I(1) &= \sum_A \bar{\Psi}_I \exp(im_A \phi_1) \\ \Psi_{II}(1) &= \sum_B \bar{\Psi}_{II} \exp(im'_B \phi_1).\end{aligned}\quad (11)$$

In view of (6) and (7) (and e.g. our treatment which formally considers that  $x_1, y_1$  and  $\rho_1$  are independent of  $R$  and  $z_1$  so that only the functional dependence of the wave function on  $z_1 = R \cos \theta_1$  need be considered), we obtain for the partial derivatives of the wavefunctions:

$$\frac{\partial \Psi_I(1)}{\partial z_1} = 2 \frac{\partial \Psi_I(1)}{\partial R} \quad \text{and} \quad \frac{\partial \Psi_{II}(1)}{\partial z_1} = -2 \frac{\partial \Psi_{II}(1)}{\partial R} \quad (12)$$

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<sup>1</sup>Note that  $\Psi_I$  means  $\Psi_{IA}$  and  $\Psi_{II}$  means  $\Psi_{IIB}$ , but we drop the  $A$  and  $B$  to avoid unnecessarily complicated symbolism in our formulas.

### 2.3 Exchange Integral

In Cartesian coordinates  $\{x, y, z\}$ , where  $z$  is on the internuclear axis with the origin at the midpoint, the numerator of Eq. (1) can now be written as [14]:

$$I = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx_1 dy_1 \left[ \Psi'_{II}{}^*(1) \frac{\partial \Psi_I(1)}{\partial z_1} - \Psi_I^*(1) \frac{\partial \Psi'_{II}(1)}{\partial z_1} \right]_{z_1=0}. \quad (13)$$

Using eqs. (11) and (12), the integrand,

$$\mathcal{I} = \Psi'_{II}{}^*(1) \frac{\partial \Psi_I(1)}{\partial z_1} - \Psi_I^*(1) \frac{\partial \Psi'_{II}(1)}{\partial z_1}$$

is rewritten as:

$$\mathcal{I} = 2 \sum \frac{\partial}{\partial R} [\bar{\Psi}_I(1) \bar{\Psi}'_{II}] \cos[(m_A - m'_B) \phi_1] \quad (14)$$

Following the conventions employed in the classic texts of Arfken [15], and Abramowitz and Stegun [16] for defining the associated Legendre polynomials  $P_\ell^m$  and the spherical harmonics  $Y_\ell^m$ , we have the following expansion:

$$P_\ell^m(\cos \theta) = \sum_{k=0}^{\ell-m} \mathcal{P}_k(\ell, m) (\cos \theta)^k (\sin \theta)^m \quad (15)$$

with  $\ell \geq m \geq 0$  and

$$\mathcal{P}_k(\ell, m) = (-1)^{(\ell-m-k)/2} \delta(\ell-m-k, \text{even}) \frac{(\ell+m+k)!}{2^\ell k! \left(\frac{\ell-m-k}{2}\right)! \left(\frac{\ell+m+k}{2}\right)!}$$

After setting  $z_1 = 0$ , and consequently  $r_1 = r'_1$ , we obtain

$$\begin{aligned} \chi_1 &= \left(1 + \frac{2}{R} r_1\right)^{g_2} \exp\left[-g_2 \left(\frac{Z_1}{R}\right)\right] \\ \chi_2 &= \exp\left[-g_1 \left(\frac{Z_2}{R}\right)\right] \end{aligned} \quad (16)$$

and

$$\begin{aligned} I &= 2 \sum_{AB} \mathcal{A}_A \mathcal{B}_B \frac{\partial}{\partial R} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx_1 dy_1 \left\{ \sum_{k_i=0} (-1)^{k_3} (R/2)^{k_1+k_3} \right. \\ &\quad \times r_1^{\gamma_A - k_1 - m_A + \delta'_B - k_3 - m'_B} \rho_1^{m_A + m'_B} \exp\left[-(\alpha_A + \beta'_B) r_1\right] \\ &\quad \times \cos[(m_A - m'_B) \phi_1] \mathcal{P}_{k_1}(\ell_A, m_A) \mathcal{P}_{k_3}(\ell'_B, m'_B) \\ &\quad \left. \times \left(1 + \frac{2}{R} r_1\right)^{g_1+g_2} \exp\left[-\frac{1}{R}(g_1 + g_2) r_1\right] \right\} \end{aligned} \quad (17)$$

with  $0 \leq k_1 \leq \ell_A - m_A$  and  $0 \leq k_3 \leq \ell'_B - m'_B$ .

### 2.4 Final Expression for the Exchange Integral

Transforming from Cartesian coordinates to cylindrical coordinates, we have:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx_1 dy_1 \rightarrow \int_0^{\infty} \rho_1 d\rho_1 \int_0^{2\pi} d\phi_1$$

For the integration of  $\mathcal{I}$  over  $\phi_1$ , we use the relation:

$$\int_0^{2\pi} d\phi_1 \cos[(m_A - m'_B)\phi_1] = \pi c(m_A - m'_B) \quad (18)$$

with

$$c(m_A - m'_B) = 2\delta(m_A - m'_B).$$

Thus, we have only one non-zero value, namely the particular case where  $m_A - m'_B = 0$  and  $c = 2$ . Combining eqs. (15), (8) and (18), the exchange integral becomes:

$$\begin{aligned} I &= \pi \sum_{AB} \mathcal{A}_A \mathcal{B}'_B c(m_A - m'_B) \sum_{k_i=0} (-1)^{k_3} \left(\frac{R}{2}\right)^{k_1+k_3} \\ &\times \mathcal{P}_{k_1}(\ell_A, m_A) \mathcal{P}_{k_3}(\ell'_B, m'_B) I_2(R) \end{aligned} \quad (19)$$

After the change of variable

$$\begin{aligned} y &= \left(\rho_1^2 + \frac{R^2}{4}\right)^{1/2} \\ d\rho_1^2 &= 2y dy, \end{aligned} \quad (20)$$

$I_2(R)$  is given by the following integral [14]:

$$\begin{aligned} I_2(R) &= 2 \int_{R/2}^{\infty} dy y^{\tau_1+1} \left(y^2 - \frac{R^2}{4}\right)^{M_1} \left(1 + \frac{2y}{R}\right)^g B(y) \\ &\times \exp\left[-\left(\alpha_A + \beta'_B + \frac{1}{R}(g_1 + g_2)\right)y\right], \end{aligned} \quad (21)$$

with

$$B(y) = \frac{1}{R}(k_1 + k_3) + \tau_1 \frac{R}{4y^2} - (\alpha_A + \beta'_B) \frac{R}{4y} + (g_1 + g_2) \left(\frac{y}{R^2} + \frac{1}{4y} - \frac{1}{R}\right). \quad (22)$$

This can be rewritten as:

$$B(y) = \sum_{j=-2}^1 b_j y^j, \quad (23)$$

where

$$\begin{aligned} b_{-2} &= \tau_1 \frac{R}{4}; & b_{-1} &= -(\alpha_A + \beta'_B) \frac{R}{4} + \frac{g}{4}; \\ b_0 &= \frac{1}{R}(k_1 + k_3) - \frac{g}{R}; & b_1 &= \frac{g}{R^2}. \end{aligned} \quad (24)$$

The accumulated list of parameters is:

$$\begin{aligned} g &= g_1 + g_2 \\ 2M_1 &= m_A + m'_B, \\ 0 \leq k_1 \leq \ell_A - m_A, & \quad 0 \leq k_3 \leq \ell'_B - m'_B, \\ \tau_1 &= \gamma_A + \delta'_B - k_1 - k_3 - 2M_1, \\ g_1 &= 1/\beta'_B, \quad g_2 = 1/\alpha_A. \end{aligned} \quad (25)$$

These are determined from atomic wave functions and physical/chemical modeling.<sup>2</sup> The basic surface integral  $I_2(R)$  includes the polarization of the wave functions through  $\chi$ , resulting in considerable complexity of the integrand.

<sup>2</sup>The reader should not be confused by the apparent redundancy in the formulations above about the actual number of parameters. For example,  $\beta'_B$  is simply the counterpart of  $\alpha_A$  for the other atom. The same relationship applies to  $\delta'_B$  and  $\gamma_A$ . The actual list of irreducible parameters for a given atom contains only  $\mathcal{A}$  and  $\alpha$ , since  $\gamma$  is a function of  $\alpha$ . The rest involve angular quantum numbers, which determine the list of indices  $k_i$ .

For a given *one-active-electron* atom-ion case, all the parameters involved in  $I_2(R)$  are known and thus the problem of evaluating  $\Delta E$  is conceptually reduced to evaluating integrals of the type  $I_2(R)$ , although doing so is far from trivial.

### 3 Method of Solution

We make the variable transformation  $Y = 2y/R$  and reduce  $I_2(R)$  to a finite sum of terms:

$$I_2(R) = 2 \sum_{i=0}^{M_1} \sum_{j=-2}^1 \binom{M_1}{i} (-1)^i b_j (R/2)^{\nu(i,j)+2i+1} I_Y(i, j, R) \quad (26)$$

where  $I_Y = I_Y(i, j, R)$  is our normalized (canonical) integral:

$$I_Y = \int_1^\infty dY e^{-s(R)Y} Y^{\nu(i,j)} (Y+1)^g \quad (27)$$

with

$$\nu(i, j) = \tau_1 + 1 + 2(M_1 - i) + j \quad \text{and} \quad 2s(R) = (\alpha_A + \beta'_B)R + g$$

Solutions for  $I_2(R)$  were derived in the work of [9]. This integral admits a few special cases leading to closed-form solutions, if  $g$  and/or  $\nu = \nu(i, j)$  are non-negative integers. The solutions in these cases are essentially linear combinations of complementary incomplete gamma functions  $\Gamma(a, z)$  [16]. However, the solutions for *arbitrary* real  $\nu$  and *arbitrary* real  $g$  (i.e. non-integer) have not been known in general. In [9], we obtained for the general case, where  $\nu$  and  $g$  are not integers but arbitrary real numbers, an ordered asymptotic series:

$$I_Y \sim \frac{2^g e^{-s}}{s} \sum_{k,l=0}^{\infty} \binom{\nu}{l} \binom{g}{k} \frac{\Gamma(k+l+1)}{2^k s^{k+l}}, \quad (28)$$

The term in  $s(R)$  as defined in (27) is proportional to  $R$ , and thus  $1/s$  serves as our ordering parameter. As shown in [9], the above is equivalent to the single summation series:

$$I_Y \sim \frac{2^g e^{-s}}{s} \sum_{k=0}^{\infty} \frac{\Gamma(g+1)}{\Gamma(g-k+1)} 2^{-k} s^{-k} {}_2F_0(k+1, -\nu; -1/s) \quad (29)$$

which is also a well-ordered series in  $1/s$  (the coefficient of  $1/s^k$  being a well-defined function of  $s$ ). It is important to note that the result in (29) also serves as a *general* analytical solution. It can still be used for small  $s$  using a Levin or Sidi transformation [17], as was also demonstrated in the work of [9].

### 4 Denominator Terms

The denominator of the Holstein-Herring formula, as written in equation (1) or for that matter in the work of Guo, Tang *et al.* [4, (c)], has the form:

$$D = 1 - 2\mathcal{D}_A \quad \text{with} \quad \mathcal{D}_A = \int_{right} |\Psi_I|^2 dV$$

However, for reasons of symmetry, as was readily shown in [9], it can also be written in the form:

$$D = \mathcal{D}_A - \mathcal{D}_B \quad \text{where} \quad \mathcal{D}_B = \int_{right} |\Psi_{II}|^2 dV. \quad (30)$$

Noting that squared expressions can be expanded as follows:

$$\left[ \sum_A \mathcal{A}_A r_1^{\gamma_A} \exp(-\alpha_A r_1) \right]^2 = \sum_{AA''} \mathcal{A}_A \mathcal{A}''_{A''} r_1^{\gamma_A + \gamma''_{A''}} \exp[-(\alpha_A + \alpha''_{A''}) r_1],$$

the expressions for the wave function  $\Psi$  about atom  $A$ , i.e. for  $-1 \leq \eta \leq 0$ , are given by:

$$\begin{aligned} \Psi_I^2 &= \left( \frac{1+\xi}{1-\eta} \right)^{2g_2} \exp[-g_2(\xi + \eta)] \sum_{AA''} \mathcal{A}_A \mathcal{A}''_{A''} r_1^{\gamma_A + \gamma''_{A''}} \exp[-(\alpha_A + \alpha''_{A''}) r_1] \\ &\quad \times P_{\ell_A}^{m_A}(\cos \theta_1) P_{\ell''_{A''}}^{m''_{A''}}(\cos \theta_1) \exp(i(m_A - m''_{A''})\phi_1), \\ \Psi_{II}^2 &= \left( \frac{1+\xi}{1-\eta} \right)^{2g_2} \exp[-g_2(\xi + \eta)] \sum_{BB''} \mathcal{B}_B \mathcal{B}''_{B''} r'_1{}^{\gamma'_B + \gamma''_{B''}} \exp[-(\beta_B + \beta''_{B''}) r'_1] \\ &\quad \times P_{\ell'_B}^{m'_B}(\cos \theta_1) P_{\ell''_{B''}}^{m''_{B''}}(\cos \theta'_1) \exp(i(m'_B - m''_{A''})\phi_1), \end{aligned} \quad (31)$$

and in the region about atom  $B$ , i.e. for  $0 \leq \eta \leq 1$ :

$$\begin{aligned} \Psi_I^2 &= \left( \frac{1+\xi}{1+\eta} \right)^{2g_2} \exp[-g_2(\xi - \eta)] \sum_{AA''} \mathcal{A}_A \mathcal{A}''_{A''} r_1^{\gamma_A + \gamma''_{A''}} \exp[-(\alpha_A + \alpha''_{A''}) r_1] \\ &\quad \times P_{\ell_A}^{m_A}(\cos \theta_1) P_{\ell''_{A''}}^{m''_{A''}}(\cos \theta_1) \exp(i(m_A - m''_{A''})\phi_1), \\ \Psi_{II}^2 &= \left( \frac{1+\xi}{1+\eta} \right)^{2g_2} \exp[-g_2(\xi - \eta)] \sum_{BB''} \mathcal{B}_B \mathcal{B}''_{B''} r'_1{}^{\gamma'_B + \gamma''_{B''}} \exp[-(\beta_B + \beta''_{B''}) r'_1] \\ &\quad \times P_{\ell'_B}^{m'_B}(\cos \theta_1) P_{\ell''_{B''}}^{m''_{B''}}(\cos \theta'_1) \exp(i(m'_B - m''_{A''})\phi_1). \end{aligned} \quad (32)$$

To calculate  $D$ , one has to integrate over the half-space containing nucleus  $B$  on the right side of the mid-plane  $\mathcal{M}$  at  $z = 0$ . To this end, we use prolate spheroidal coordinates, but for the considered domain of integration, we must take:

$$1 \leq \xi < +\infty, \quad 0 \leq \eta < 1, \quad 0 \leq \phi < 2\pi \quad (33)$$

We can write:

$$\int_0^{2\pi} d\phi_1 \cos[(m_A - m''_{A''})\phi_1] = \pi c(m_A - m''_{A''}) \quad (34)$$

#### 4.1 D Integrals

$$\begin{aligned} \mathcal{D}_A &= \frac{\pi}{8} R^3 \sum_{AA''} \mathcal{A}_A \mathcal{A}''_{A''} c(m_A - m''_{A''}) \left( \frac{R}{2} \right)^{\gamma_A + \gamma''_{A''}} \\ &\quad \times \sum_{k_i=0} \mathcal{P}_{k_1}(\ell_A, m_A) \mathcal{P}_{k_3}(\ell''_{A'}, m''_{A''}) \\ &\quad \times \left\{ \int_1^\infty d\xi \int_0^1 d\eta (\xi^2 - \eta^2)(\xi\eta + 2)^{k_1+k_4} (\xi + \eta)^{\tau_A} (\xi^2 + \eta^2 - \xi^2\eta^2 - 2\xi\eta - 4)^{M''_A} \right. \\ &\quad \left. \exp[-\frac{R}{2}(\alpha_A + \alpha''_{A''})(\xi + \eta)] \left( \frac{1+\xi}{1+\eta} \right)^{2g_1} \exp[-g_1(\xi - \eta)] \right\} \end{aligned} \quad (35)$$

and

$$\begin{aligned}
\mathcal{D}_B = & \frac{\pi}{8} R^3 \sum_{BB''} \mathcal{B}_B \mathcal{B}''_{B''} c(m'_B - m''_{B''}) \left(\frac{R}{2}\right)^{\gamma_{B'} + \gamma''_{B''}} \\
& \times \sum_{k_i=0} \mathcal{P}_{k_1}(\ell'_B, m'_B) \mathcal{P}_{k_3}(\ell''_B, m''_{B''}) \\
& \times \left\{ \int_1^\infty d\xi \int_0^1 d\eta (\xi^2 - \eta^2)(\xi\eta)^{k_1+k_4} (\xi - \eta)^{\tau_B} (\xi^2 + \eta^2 - \xi^2\eta^2 - 2\xi\eta - 4)^{M''_B} \right. \\
& \left. \exp\left[-\frac{R}{2}(\beta'_B + \beta''_{B''})(\xi - \eta)\right] \left(\frac{1+\xi}{1+\eta}\right)^{2g_1} \exp[-g_1(\xi - \eta)] \right\}
\end{aligned} \tag{36}$$

where

$$\begin{aligned}
2M''_A &= m_A + m''_{A''} \\
2M''_B &= m_B + m''_{A''} \\
\tau_A &= \gamma_A + \gamma''_{A''} - k_1 - k_4 - 2M''_A \\
\tau_B &= \gamma'_B + \gamma''_{B''} - k_1 - k_4 - 2M''_B \\
0 &\leq k_1 \leq \ell'_B - m'_B \\
0 &\leq k_4 \leq \ell''_{B''} - m''_{B''}
\end{aligned}$$

## 4.2 Special Case: $\ell_i = m_i = 0$

This corresponds in particular to the interesting situation of the exchange energy for the ground states  $^2\Sigma_g^+$ ,  $^2\Sigma_u^+$  of alkali cation ions  $M_2^+$ . As in all special cases, this has to be handled separately, although it is completely analogous to the general case. Consequently, we only outline the final results. The parameters  $k_1$ ,  $k_3$  and  $M_1$  involved in the general expression for  $I_2(R)$  [eq. (21)] are all equal to zero in this special case. Thus,

$$\begin{aligned}
I_2(R) = & 2 \int_{R/2}^\infty dy y^{\tau_1+1} \left(1 + \frac{2y}{R}\right)^{g_1+g_2} B(y) \\
& \times \exp\left[-\left(\alpha_A + \beta'_B + \frac{1}{R}(g_1 + g_2)\right)y\right]
\end{aligned} \tag{37}$$

with

$$B(y) = \tau_1 \frac{R}{4y^2} - (\alpha_A + \beta'_B) \frac{R}{4y} + (g_1 + g_2) \left(\frac{y}{R^2} + \frac{1}{4y} - \frac{1}{R}\right) \tag{38}$$

and  $\tau_1 = \gamma_A + \delta'_B$ ,  $g_1 = 1/\beta'_B$ ,  $g_2 = 1/\alpha_A$ . This is indeed the result of (21) with  $k_1 = k_3 = M_1 = 0$ . Using the parameters  $m''_A = m''_B = k_1 = k_4 = 0$  in eq. (35) for  $\mathcal{D}_A$ , we obtain as before the denominator term of the form (30) where

$$\mathcal{D}_A = \frac{\pi}{4} R^3 \sum_{AA''} \mathcal{A}_A \mathcal{A}''_{A''} \left(\frac{R}{2}\right)^{\gamma_A + \gamma''_{A''}} D_A \tag{39}$$

where  $D_A$  is a double integral given by:

$$D_A = \int_1^\infty d\xi \int_0^1 d\eta (\xi^2 - \eta^2) (\xi + \eta)^{\tau_A} e^{-S(\xi+\eta)} \left(\frac{1+\xi}{1+\eta}\right)^{2g_1} e^{-g_1(\xi-\eta)}, \tag{40}$$

with  $S = \frac{R}{2}(\alpha_A + \alpha''_{A''})$

Just as for  $I_2(R)$ , we now bring  $D_A$  into a normal form with the aid of the variable transformation  $X = \xi + \eta$ :

$$D_A = \int_0^1 d\eta \left( \frac{e^\eta}{\eta+1} \right)^{2g_1} \left\{ \int_{1+\eta}^\infty dX X^{\gamma+2} e^{-pX} (X+C)^{2g_1} - 2\eta \int_{1+\eta}^\infty dX X^{\gamma+1} e^{-pX} (X+C)^{2g_1} \right\} \quad (41)$$

We therefore have two inner integrals of the form:

$$I_X = \int_{1+\eta}^\infty dX X^N e^{-pX} (X+C)^{2g_1} \quad (42)$$

where  $C = 1 - \eta$ ,  $p = S + g_1$  and  $N = \gamma + 1$  or  $N = \gamma + 2$ . Note that the integral  $I_X$  greatly resembles  $I_Y$ , the canonical form of  $I_2(R)$ . As in  $I_2(R)$ , there are no known general solutions unless  $N$  or  $2g_1$  is equal to  $0, 1, 2, \dots$ . In the case where  $2g_1$  is a positive integer, we can expand  $(X+C)^{2g_1}$  as a binomial series and integrate term-by-term. As in the special cases for  $I_2(R)$ , the solution is expressible in terms of the incomplete gamma function. We proceed as with  $I_2(R)$ :

1. we obtain an *ordered* asymptotic expansion and
2. attempt to collapse the result into something simpler.

To obtain the asymptotic expansion of

$$I_X = \frac{e^{-p(\eta+1)}}{p} \int_0^\infty dt e^{-t} \left( 1 + \eta + \frac{t}{p} \right)^N \left( 2 + \frac{t}{p} \right)^{2g_1} \quad (43)$$

The solutions are found in terms of hypergeometric functions, most of which can be collapsed into closed-form algebraic expressions as shown in [9]. These provided a good benchmark for numerical analysis. In general, we use quadrature techniques suitably applied to these analytical forms of these integrals and compare the numerical results from those of our analytical solutions using the multiple precision of Computer Algebra.

### 4.3 Asymptotic Formulas for the case $R \rightarrow \infty$

After setting  $z_1 = 0$ , and consequently  $Z_1 = Z_2 = R/2$ , the polarization terms of eq. (10) become:

$$\begin{aligned} \chi_1 &= 2^{g_2} \exp\left[-\frac{g_2}{2}\right] \\ \chi_2 &= 2^{g_1} \exp\left[-\frac{g_1}{2}\right] \end{aligned} \quad (44)$$

and the exchange integral becomes:

$$\begin{aligned} I &= \pi \sum_{AB} \mathcal{A}_A \mathcal{B}_B c(m_A - m'_B) 2^{g_1+g_2} \exp\left[-\frac{1}{2}(g_1 + g_2)\right] \\ &\times \sum_{k_i=0} (-1)^{k_3} \left(\frac{R}{2}\right)^{k_1+k_3} \mathcal{P}_{k_1}(\ell_A, m_A) \mathcal{P}_{k_3}(\ell'_B, m'_B) I_2(R) \end{aligned} \quad (45)$$

where

$$\begin{aligned}
I_2(R) &= \int_0^\infty d\rho^2 \left( \rho^2 + \frac{R^2}{4} \right)^{\tau_1/2} \rho^{2M_1} \\
&\times \exp \left[ -(\alpha_A + \beta'_B) \left( \rho^2 + \frac{R^2}{4} \right)^{1/2} \right] \\
&\times \left\{ \frac{1}{R} (k_1 + k_3) + \tau_1 \frac{R}{4(\rho^2 + \frac{R^2}{4})} - (\alpha_A + \beta'_B) \frac{R}{4 \left( \rho^2 + \frac{R^2}{4} \right)^{1/2}} \right\}
\end{aligned} \tag{46}$$

If, as Chibisov and Janev did, we take the derivative of only the exponential term in (17), we obtain the following approximate form for  $I_2$ :

$$\begin{aligned}
I_2(R) &= -(\alpha_A + \beta'_B) \int_0^\infty d\rho^2 \left( \rho^2 + \frac{R^2}{4} \right)^{\tau_1/2} \rho^{2M_1} \\
&\times \frac{R}{4 \left( \rho^2 + \frac{R^2}{4} \right)^{1/2}} \exp \left[ -(\alpha_A + \beta'_B) \left( \rho^2 + \frac{R^2}{4} \right)^{1/2} \right]
\end{aligned} \tag{47}$$

#### 4.4 Asymptotic Formulas $R \rightarrow \infty$ for the special case $\ell_i = m_i = 0$

We obtain for  $I$ :

$$I = \pi 2^{1+g_1+g_2} \exp\left[-\frac{1}{2}(g_1 + g_2)\right] \sum_{AB} \mathcal{A}_A \mathcal{B}_B \tag{48}$$

$$\times \frac{\partial}{\partial R} \int_{-\infty}^\infty \int_{-\infty}^\infty dx_1 dy_1 r_1^{\gamma_A + \delta'_B} \exp[-(\alpha_A + \beta'_B) r_1]$$

$$I = \pi \sum_{AB} \mathcal{A}_A \mathcal{B}_B 2^{1+g_1+g_2} \exp\left[-\frac{1}{2}(g_1 + g_2)\right] I_2(R) \tag{49}$$

where  $I_2(R)$  is given by:

$$\begin{aligned}
I_2(R) &= \int_0^\infty d\rho^2 \left( \rho^2 + \frac{R^2}{4} \right)^{(\gamma_A + \delta'_B)/2} \\
&\times \exp \left[ -(\alpha_A + \beta'_B) \left( \rho^2 + \frac{R^2}{4} \right)^{1/2} \right] \\
&\times \left\{ (\gamma_A + \delta'_B) \frac{R}{4(\rho^2 + \frac{R^2}{4})} - (\alpha_A + \beta'_B) \frac{R}{4 \left( \rho^2 + \frac{R^2}{4} \right)^{1/2}} \right\}
\end{aligned} \tag{50}$$

or in the case where we take the derivative of only the exponential term, we obtain:

$$\begin{aligned}
I_2(R) &= -(\alpha_A + \beta'_B) \int_0^\infty d\rho^2 \left( \rho^2 + \frac{R^2}{4} \right)^{(\gamma_A + \delta'_B)/2} \\
&\times \frac{R}{4 \left( \rho^2 + \frac{R^2}{4} \right)^{1/2}} \exp \left[ -(\alpha_A + \beta'_B) \left( \rho^2 + \frac{R^2}{4} \right)^{1/2} \right]
\end{aligned} \tag{51}$$



## 5 Results

### 5.1 Analytical Asymptotic Exchange Energy Formulas

Eqs. (45-46) provide analytical expressions for the asymptotic form of the exchange energy corresponding to the two indistinguishable separated limits  $M^+ + M(n\ell)$  and  $M(n\ell) + M^+$ , where  $M$  is a one-active electron atom and  $\ell = 0, 1$ . To proceed, we use computer algebra to expand the solutions of eqs. (19-25) which are given in eqs. (26-29), and the leading terms of the resulting asymptotic series are gathered in Table 1. They correspond to an atomic wavefunction written in the general form:

$$\phi_{n,\ell} = \mathcal{A} r^\gamma e^{-\alpha r}. \quad (52)$$

Apart for  $\Sigma$  states dissociating adiabatically to  $M^+ + M(np)$  ( $\Sigma(np)$ ), these formulas are identical to the well-known ones obtained by Chibisov and Janev with  $\gamma = \frac{1}{\alpha} - 1$ , where  $\alpha$  is related to the electronic energy  $E_{n\ell}$  for the  $n\ell$  state under consideration by  $\alpha = \sqrt{-2E_{n\ell}}$ . This energy  $E_{n\ell}$  can be estimated theoretically or experimentally (an average is made with the spin-orbit  $J$  components if the case arises). For example, in the case of Caesium:

$$\begin{aligned} E_{6s} &= -31406.47 \text{ cm}^{-1} & \Rightarrow & \alpha_{ns} = 0.535 \text{ a.u.} \\ E_{6p} &= -(31406.47 - 11547.63) \text{ cm}^{-1} & \Rightarrow & \alpha_{np} = 0.425 \text{ a.u.} \\ & -11547.63 = \frac{2E_{6p1/2} + 4E_{6p3/2}}{6} \end{aligned}$$

For  $\Sigma(np)$  states, the present formulas reduce to those of Chibisov and Janev for  $1 \gg \frac{1}{\alpha^2 R}$ .

### 5.2 Some Illustrative Results

#### Hydrogen Molecular Ion $H_2^+$

First we check that our asymptotic formulas provide at least the first term of the known results for the exchange energy difference between the  $^2\Lambda_u$  and  $^2\Lambda_g$  states of  $H_2^+$  dissociating into  $H^+ + H(n\ell)$ . As a matter of fact, one obtains for the ground state:

$$E_{\text{exchange}} [(1)^2\Sigma_{u,g}^+] = \frac{2R}{e} e^{-R} \quad (53)$$

(Note that  $E_{\text{exchange}} = \Delta E ((1)^2\Sigma_u^+, (1)^2\Sigma_g^+) / 2$ ).

For  $\Sigma$  states dissociating into  $H^+ + H(2\ell)$ , we obtain the first two terms for  $E_{\text{exchange}}$

$$E_{\text{exchange}} [(2)^2\Sigma_{u,g}^+] = \frac{R^3}{8e^2} e^{-R/2} \left(1 - \frac{4}{R}\right) \quad (54)$$

after diagonalizing the exchange energy matrix of order 2, built up in the basis  $\{2s, 2p_z\}$  of hydrogenic functions. Eq. (54) is indeed the correct result corresponding to the first application of the Holstein Herring formula to an excited state [5, eq. (22)], obtained from a refinement of the Herring function worked out by Bardsley *et al.* [3, (d)].

For  $\Pi$  states dissociating into  $H^+ + H(2p)$ , we obtain:

$$E_{\text{exchange}} [(1)^2\Pi_{u,g}] = \frac{R^2}{8e^2} e^{-R/2} \quad (55)$$

Symmetry	$n\ell$	$M_1$	$k_1$	$k_3$	$\tau_1$	$E_{\text{Exchange}}$
$\Sigma_{g,u}^+$	$ns$	0	0	0	$2\gamma$	$\frac{\mathcal{A}_{ns}^2}{4} \left(\frac{4}{e}\right)^{1/\alpha} \left(\frac{R}{2}\right)^{2\gamma+1} e^{-R\alpha}$
$\Sigma_{g,u}^+$	$np$	0	1	1	$2\gamma - 2$	$\frac{3\mathcal{A}_{np}^2}{4} \left(\frac{4}{e}\right)^{1/\alpha} \left(\frac{R}{2}\right)^{2\gamma+1} \frac{e^{-R\alpha}}{1 + \frac{1}{\alpha^2 R}}$
$\Pi_{g,u}$	$np$	1	0	0	$2\gamma - 2$	$\frac{3\mathcal{A}_{np}^2}{4} \left(\frac{4}{e}\right)^{1/\alpha} \left(\frac{R}{2}\right)^{2\gamma+1} \frac{e^{-R\alpha}}{\alpha R}$

**Table 1:** Asymptotic exchange energy formulas for one-active electron cases  $M^+ + M(n\ell)$ . For definitions of  $M_1$ ,  $k_1$ ,  $k_3$  and  $\tau_1$ , see text. ( $\gamma = \frac{1}{\alpha} - 1$ )

which is indeed the correct leading term. The result in eq.(55) is notable because the leading term is smaller by one power of  $R$  than the result of eq.(54) and therefore more elusive: it could not be obtained from the refined Herring function of Bardsley *et al.* [3, (d)]. These results give us confidence in the polarization functions of Chibisov and Janev [13].

### 5.3 Alkali Cations $M_2^+$

For one-active electron diatomic ions, we illustrate the method with calculations for the heavier cations  $M_2^+$  with  $M = K, Rb$  and  $Cs$ , due to our recent *ab initio* investigations of these species [10–12]. These investigations were performed treating  $M_2^+$  ions as one-active electron systems. Non-empirical pseudopotentials and effective core potentials were used to describe interactions between the active electron and the atomic cores  $M^+$  as well as to take into account core polarization effects. Contracted Gaussian basis sets were used.

Numerical values for the exchange energy have been calculated for the  $^2\Sigma_u^+$  Van der Waals states, corresponding to the interactions  $M^+ + M(n\ell)$  with  $M, n, \ell = \{K, 4, \ell\}; \{Rb, 5, \ell\}, \{Cs, 6, \ell\}$  and  $\ell$  is 0 or 1 ( $s$  or  $p$  functions). As a matter of fact, among the 6 states  $^2\Lambda_{g,u}^+$  ( $\Lambda = \Sigma, \Pi$ ) corresponding to these dissociating limits, only the  $^2\Sigma_u^+$  states are bound with small wells at long range.

It should be emphasized that present evaluations of exchange energies are expected to be specially adequate to describe such situations. This justifies our choice for the presentation of our results. Due to the lack of experimental data for alkali dimer cations, *ab initio* values for the exchange energy are chosen as references in the present paper. Nevertheless it should be kept in mind that, while expected to be accurate, these values are not the exact experimental ones.

To perform long-range evaluations of exchange energies, we used the asymptotic atomic parameters shown in Table 2. As mentioned before, the irreducible list of parameters requires  $\mathcal{A}$  and  $\alpha$  and the parameters  $\alpha$  are derived according to our discussion of Section 5.1.

Atom	$\alpha_{ns}$	$\alpha_{np}$	$\mathcal{A}_{ns}$	$\mathcal{A}_{np}$
K	0.565	0.448	0.59848	0.13356
Rb	0.554	0.437	0.56945	0.12055
Cb	0.535	0.425	0.51020	0.10739

**Table 2:** Parameters for Alkali systems  $M(n\ell)$ .

For the ground state  $^2\Sigma_u^+$  of the three cations, we compare our present values with those evaluated

from the formulas of Chibisov and Janev [13] and Johann *et al.* [4, (d)]. Our long-range predictions were seen to be in an overall good agreement with the *ab initio* values, not only for values of  $R$  larger than the bond length  $R_e$  predicted from *ab initio* calculations, but also for values of  $R$  smaller than  $R_e$ , down to approximately  $\{R_e - 2a_o\}$ .

We display comparative results in Fig. 1 for  $\text{Cs}_2^+$  chosen as an example. The vertical dotted line represents the position of the equilibrium distance for the  $^2\Sigma_u^+$  state. Our present results from eqs. (19-25) are seen to be very close to those obtained from the corresponding asymptotic form (see Table 1). On the scale of the figure, they are indistinguishable.

For more quantitative comparisons, we choose to present also the results as differences between the *ab initio* and long range values. This is done in Fig. 2 for  $\text{Cs}_2^+$ . As expected, the differences increase for decreasing values of  $R$  and they decrease monotonically with increasing values of  $R$ . They practically vanish at  $R \approx 30 a_o$  for the three cations.

Around  $R \approx R_e$ , our present results agree better with the *ab initio* data than did the previous ones by Chibisov and Janev [13] and by Johann *et al.* [4, (d)]. This holds also for  $\text{K}_2^+$  and  $\text{Rb}_2^+$ . Nevertheless, it should be noted that for  $\text{K}_2^+$  the predictions by Johann *et al.* [4, (d)] are in better agreement with the *ab initio* values than ours in the range  $25a_o < R < 28a_o$ . The corresponding figures for  $\text{K}_2^+$  and  $\text{Rb}_2^+$  were seen to be very similar to Figs. 1 and 2, in fact virtually identical, which is why they are not displayed here.

The results for the excited state  $(2)^2\Sigma_u^+$  dissociating into  $\text{M}^+ + \text{M}(np_z)$  are displayed in Figs. 3-4 for  $\text{Cs}_2^+$ , together with the results of Chibisov and Janev [13]. From Fig. 3, it is apparent that there are significant differences between the results from our eqs. (19-25) and the corresponding asymptotic form (see Table 1). They increase with decreasing values of  $R$  and, as could be expected, our results from eqs. (19-25) better reproduce the *ab initio* values than do the asymptotic ones of Table 1, in the region  $R \lesssim R_e$ .

Fig. 4 shows differences between the *ab initio* data and the various long-range values. The agreement is not as good as for the ground state. Around the  $R_e$  value, our results from eqs. (19-25) are seen to be the best ones, and they are in reasonably good agreement with the *ab initio* values. The present asymptotic values as well as those of Chibisov and Janev are in good agreement with the *ab initio* data for the region  $R \gtrsim 33 a_o$ . Oddly enough, we note that at very large distances, the asymptotic form of Table 1 is actually better than the results of eqs. (19-25). A possible explanation might be that the *ab initio* reference is a bit faulty at very large distances. This result is not *exact* and the larger the distances, the more the *ab initio* results lose precision. It could also be that the leading term of Table 1 is the only physically representative term of the true asymptotic series and that the validity of the polarization functions of Chibisov and Janev is limited to only that leading term [see the discussion in our introduction].

## 6 Conclusions

We have analyzed and reduced a general (quantum-mechanical) atom-ion diatomic exchange energy formulation into fundamental mathematical forms. The solutions have been worked out using asymptotic expansions in inverse powers of large internuclear distance  $R$ . Numerical schemes based on quadratures for the resulting integrals have been developed and tested by comparison with the analytical results.

The resulting asymptotic expansions involving multiple summations where the number of summation indices were most often reduced using algorithms for collapsing sums into closed form

expressions in terms of hypergeometric functions. In the end, we obtained simple forms for the leading terms of the asymptotic expansions of the exchange energies for the ground and excited states, which are in very good agreement with *ab initio* calculations starting from the intermediate range (e.g. bond-length) to larger internuclear distances.

In view of the elusive nature of the quantities to be calculated i.e. that the exchange energy is an exponentially vanishing function of  $R$ , we have avoided “brute-force” techniques and presented solutions which are “natural”, i.e. resulting from the natural mathematical properties of the very quantities we analyzed. The analytical results helped verify the accuracy of our quadrature schemes and ensured double precision accuracy in the final computations. The resulting codes can be used with confidence for a variety of physical/chemical calculations. Moreover, the analytical results can be used within a large study of atmospheres (stellar or otherwise).

Our numerical comparison of the *ab initio* calculations with the results of the Holstein-Herring method vindicates the discussion following eq. (2), namely, that the best result is from the first leading non-vanishing term of the asymptotic expansions of the surface integral and determining that particular coefficient as accurately as possible. In practice, the addition of the next term of the asymptotic expansion is actually a nuisance unless the internuclear distance  $R$  is large enough, and in the long-range regime, the next term is hardly needed anyway.

Thus, the exchange energies can be effectively expressed as very simple closed-form semi-analytical formulas, as shown in Table 1, whose leading (scalar) coefficient is determined by the accuracy of the (atomic) basis set expansion used. In the cases examined, it is found that the resulting formulas work remarkably well for long-range interactions, especially in regimes beyond the capacity of *ab initio* calculations, and also work surprisingly well for mid-range distances near the equilibrium separation. As can be seen in our figures, our results are more accurate than those of Chibisov and Janev and are slightly more accurate than those of Tang and Toennies and their co-workers. More significantly, we have obtained accurate results for exchange splittings between excited states, which Tang and Toennies and their co-workers do not have<sup>3</sup>.

Work is underway to extend the results presented here will be extended to the *two-active* electron case.

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<sup>3</sup>With regards to the physical aspects of the molecules themselves, we realize that we made the approximation that the nuclei were clamped, i.e. fixed in space. A different picture arises when the movement of nuclei is considered. The mere movement of the nuclei breaks the symmetry under exchange of nuclei and thereby leads to a localization of the states, as has been discussed by Esry and Sadeghpour [18].

## References

- [1] E. E. Nikitin and S. Ya. Umanskii, *Theory of slow atomic Collisions*, Springer Series in Chemical Physics, **30**, Springer, Berlin, (1984).
- [2] B. Bussery, and S. Ya. Umanskii, M. Aubert-Frécon, O. Bouty, J. Chem. Phys. **101**, p. 416 (1994).
- [3] (a) T. Holstein, *Mobilities of positive ions in their parent gases*, J. Phys. Chem. **56**, pp. 832-836 (1952); (b) T. Holstein, Westinghouse Research Report 60-94698-3-R9 (unpublished, 1955); (c) C. Herring, *Critique of the Heitler-London Method of Calculating Spin Couplings at Large Distances*, Rev. Mod. Phys. **34**, pp. 631-645 (1962); (d) J. N. Bardsley, T. Holstein, B. R. Junker, and S. Sinha, *Calculations of ion-atom interactions relating to resonant charge-transfer collisions*, Phys. Rev. A **11**, pp. 1911-1920 (1975); (e) C. Herring and M. Flicker, *Asymptotic Exchange Coupling of Two Hydrogen Atoms*, Phys. Rev. [Sect.] A **134**, pp. 362-366 (1964).
- [4] (a) K.T. Tang, J.P. Toennies, and C.L. Yiu, J. Chem. Phys. **92**, p. 7441 (1990); (b) K.T. Tang, J.P. Toennies, and C.L. Yiu, J. Chem. Phys. **94**, p. 7266 (1991); (c) G.L. Guo, K.T. Tang, J.P. Toennies and C.L. Yiu, J. Chem. Phys. **98**, pp. 8777-8784 (1993); (d) Ch. Johann, S. H. Patil, K. T. Tang and J. P. Toennies, *Asymptotic theory for the  $^2\Sigma_u$  Van Der Waals potentials of alkali dimer cations*, Chem. Phys. Lett. **295**, pp. 158-166 (1998); (e) U. Kleinekathöfer, T. I. Sachse, K.T. Tang, J.P. Toennies, and C.L. Yiu, *Three-body Exchange Energies in  $H_3$  and  $He_3$  calculated by the Surface Integral Method*, J. Chem. Phys. **113**, pp. 948-956 (2000).
- [5] T. C. Scott, A. Dalgarno, and J. D. Morgan III, *Exchange Energy of  $H_2^+$  Calculated from Polarization Perturbation Theory and the Holstein-Herring Method*, Phys. Rev. Lett. **67**, pp. 1419-1422 (1991).
- [6] T. C. Scott, J. F. Babb, A. Dalgarno, and J. D. Morgan III, *The Calculation of Exchange Forces: General Results and Specific Models*, J. Chem. Phys. **99**, pp. 2841-2854 (1993).
- [7] T. C. Scott, J. F. Babb, A. Dalgarno, and J. D. Morgan III, *Resolution of a Paradox in the Calculation of Exchange Forces for  $H_2^+$* , Chem. Phys. Lett. **203**, pp. 175-183 (1993).
- [8] J. D. Morgan III and B. Simon, Intern. J. Quantum Chem. **17**, p. 1143 (1980).
- [9] T. C. Scott, M. Aubert-Frécon and D. Andrae, *Asymptotics of Quantum Mechanical Atom-Ion Systems*, AAEECC (Applicable Algebra in Engineering, Communication and Computing), **13**, pp. 233-255 (2002).
- [10] S. Magnier, M. Aubert-Frécon, JQSRT (Journal of Quantitative Spectroscopy and Radiation Transfer), **78**, pp. 217-225 (2003).
- [11] A. Jraij, A. R. Allouche, M. Korek, M. Aubert-Frécon, Chem. Phys. **290**, pp. 129-136 (2003).

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- [12] A. Jraij, *Etude théorique de la structure et des propriétés électroniques de différents composés d'alcalins*, Thesis no. 47-2003, University of Lyon 1, France (2003); A. Jraij, A. R. Allouche, M. Korek, M. Aubert-Frécon, Chem. Phys. submitted (2004).
  - [13] M. I. Chibisov and R. K. Janev, *Asymptotic Exchange Interactions in Ion-Atom Systems*, Phys. Rep. **166**, pp. 1-87 (1988).
  - [14] O. Bouty, *Energie d'interaction d'échange à grande distance internucléaire dans une molécule diatomique*, Thesis no. 100-94, University of Lyon 1, France (1994).
  - [15] G. B. Arfken, *Mathematical Methods for Physicists*, 2nd ed., Academic Press, New York (1970).
  - [16] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (9th printing), Dover, New York (1970).
  - [17] J. Grotendorst, *A Maple Package for Transforming Series, Sequences and Functions*, Comput. Phys. Commun. **67**, pp. 325-342 (1991).
  - [18] B. D. Esry and H. R. Sadeghpour, *Adiabatic formulation of heteronuclear hydrogen molecular ion*, Phys. Rev. A **60**, pp. 3604-3617 (1999).

## Figure Captions

**Fig. 1** Exchange energy for the  $(1)^2\Sigma_u^+$  state of  $\text{Cs}_2^+$ .

**full line:** *ab initio* values;

**dashed line:** eqs.(19-25);

**points x:** asymptotic values (see Table 1);

**points o:** Johann *et al.* [ [4, (d)]] values

**dotted line:** Chibisov and Janev (CJ) values.

The dotted vertical line represents the position of  $R_e$  for the  $(1)^2\Sigma_u^+$  state.

**Fig. 2** Differences between *ab initio* and long-range values of the exchange energy for the  $(1)^2\Sigma_u^+$  state of  $\text{Cs}_2^+$ .

**full line:** eqs.(19-25);

**dashed line:** asymptotic values (see Table 1);

**dotted line:** CJ values [4, (d)];

**dash-dotted line:** Johann *et al.* [ [4, (d)]] values

The dotted vertical line represents the position of  $R_e$  for the  $(1)^2\Sigma_u^+$  state.

**Fig. 3** Exchange energy for the  $(2)^2\Sigma_u^+$  state of  $\text{Cs}_2^+$ .

**full line:** *ab initio* values;

**dashed line:** eqs.(19-25);

**dotted line:** asymptotic values (see Table 1);

**dash-dotted line:** CJ values [4, (d)];

The dotted vertical line represents the position of  $R_e$  for the  $(2)^2\Sigma_u^+$  state.

**Fig. 4** Differences between *ab initio* and long-range values of the exchange energy for the  $(2)^2\Sigma_u^+$  state of  $\text{Cs}_2^+$ .

**full line:** eqs.(19-25);

**dashed line:** asymptotic values (see Table 1);

**dotted line:** CJ values [4, (d)];

The dotted vertical line represents the position of  $R_e$  for the  $(2)^2\Sigma_u^+$  state.

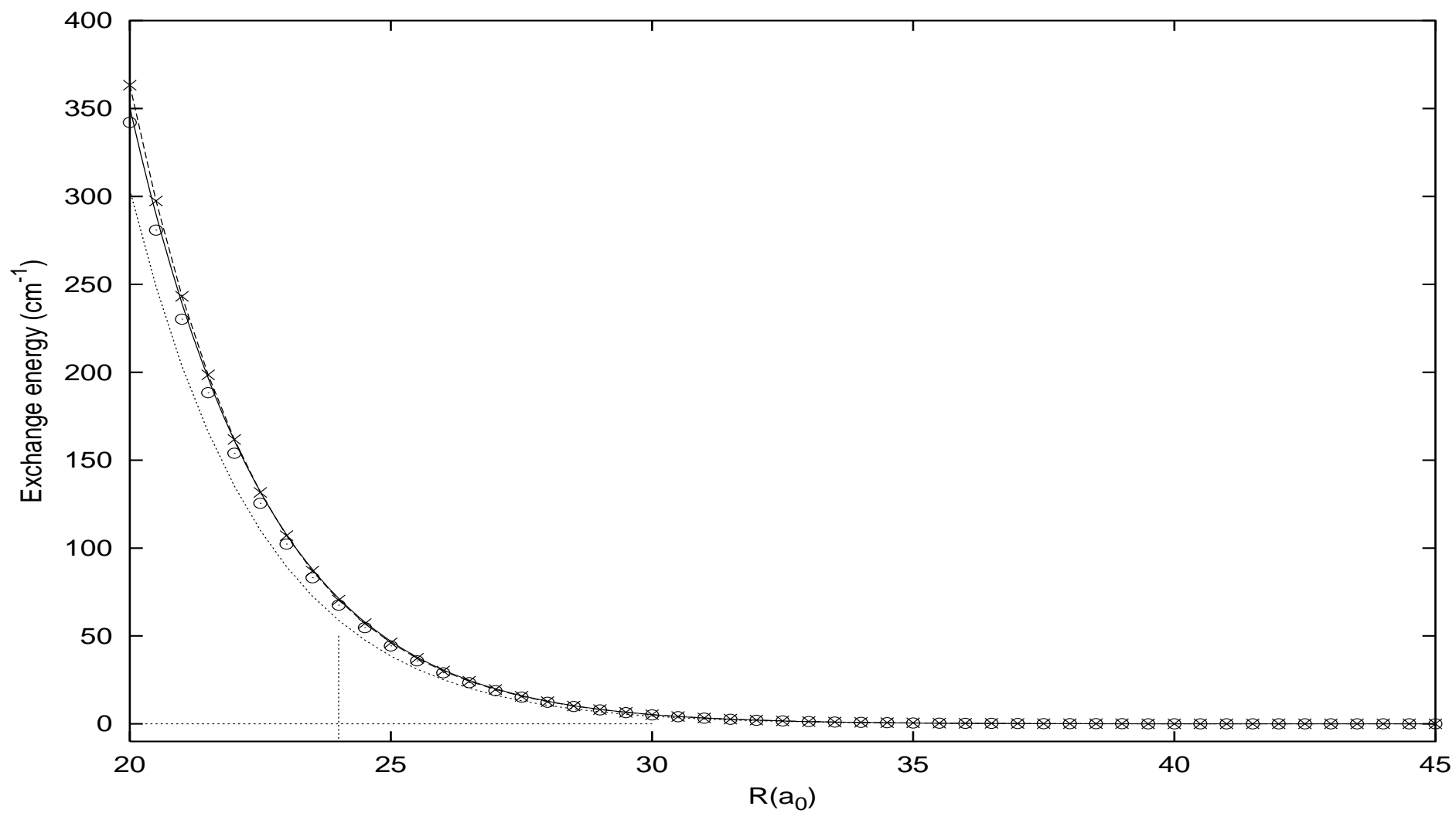


Figure 1: Exchange energy for the  $(1)^2\Sigma_u^+$  state of  $\text{Cs}_2^+$



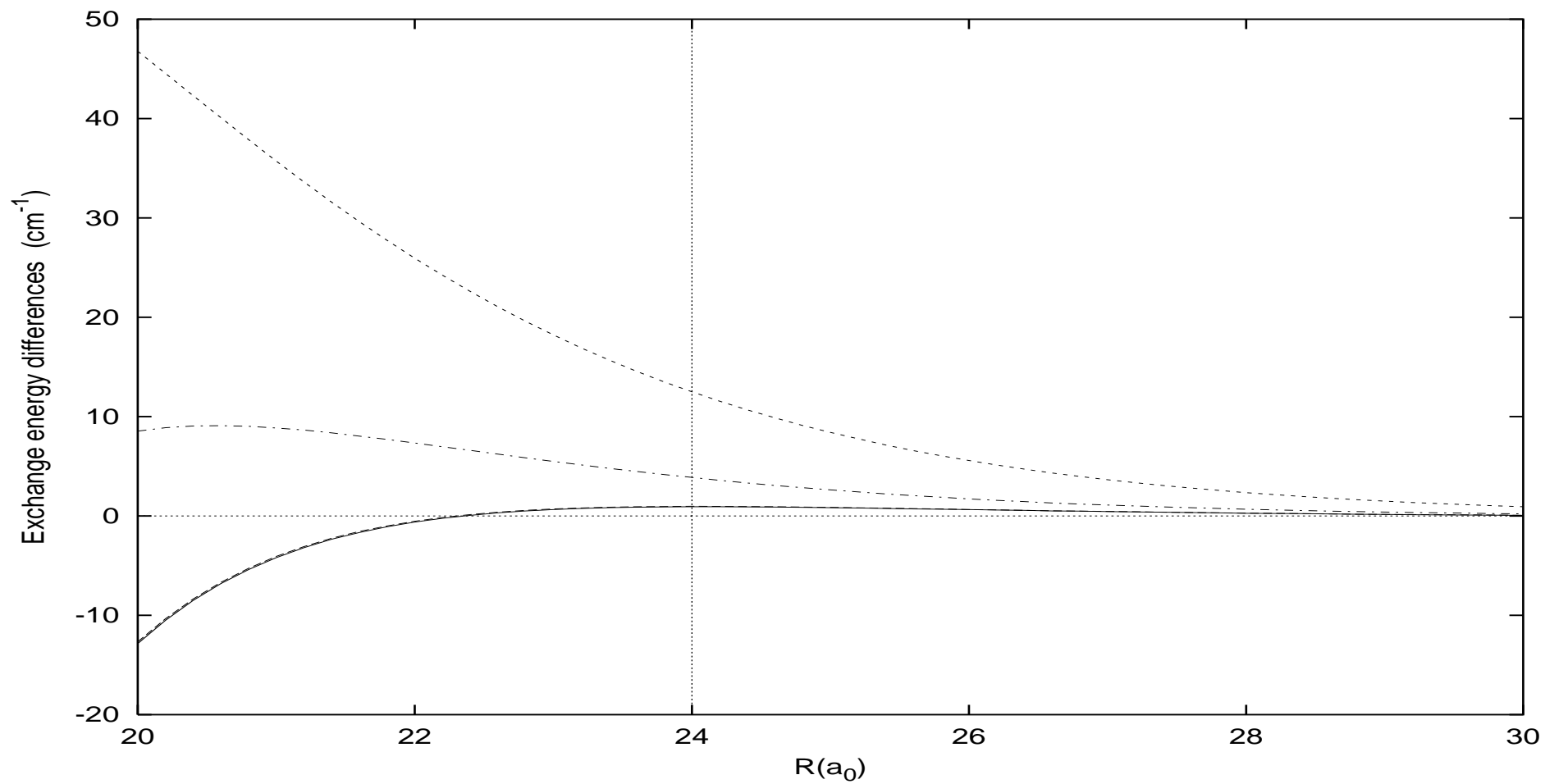


Figure 2: Differences between *ab initio* and long-range values of the exchange energy for the  $(1)^2\Sigma_u^+$  state of  $\text{Cs}_2^+$

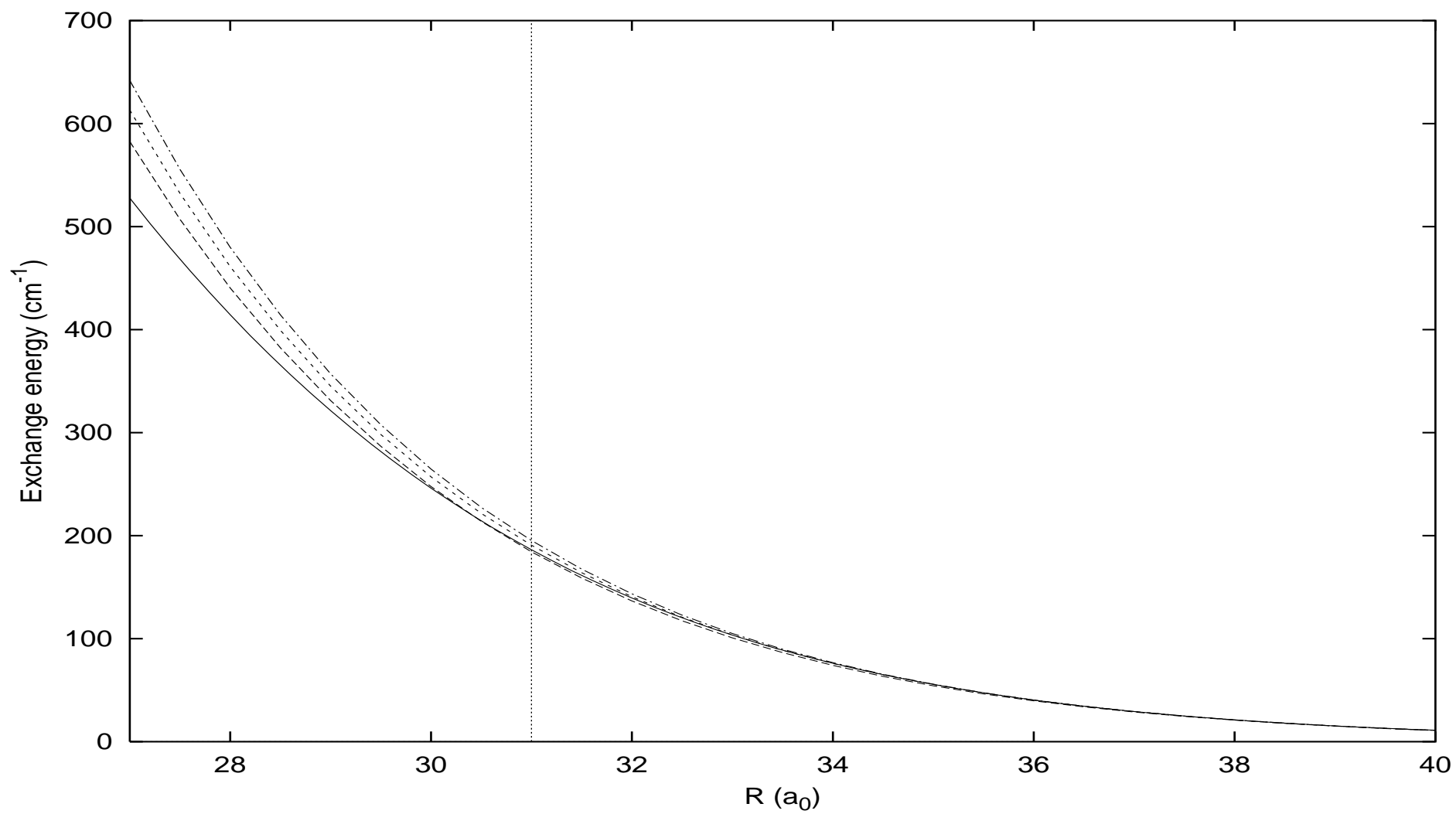


Figure 3: Exchange energy for the  $(2)^2\Sigma_u^+$  state of  $\text{Cs}_2^+$

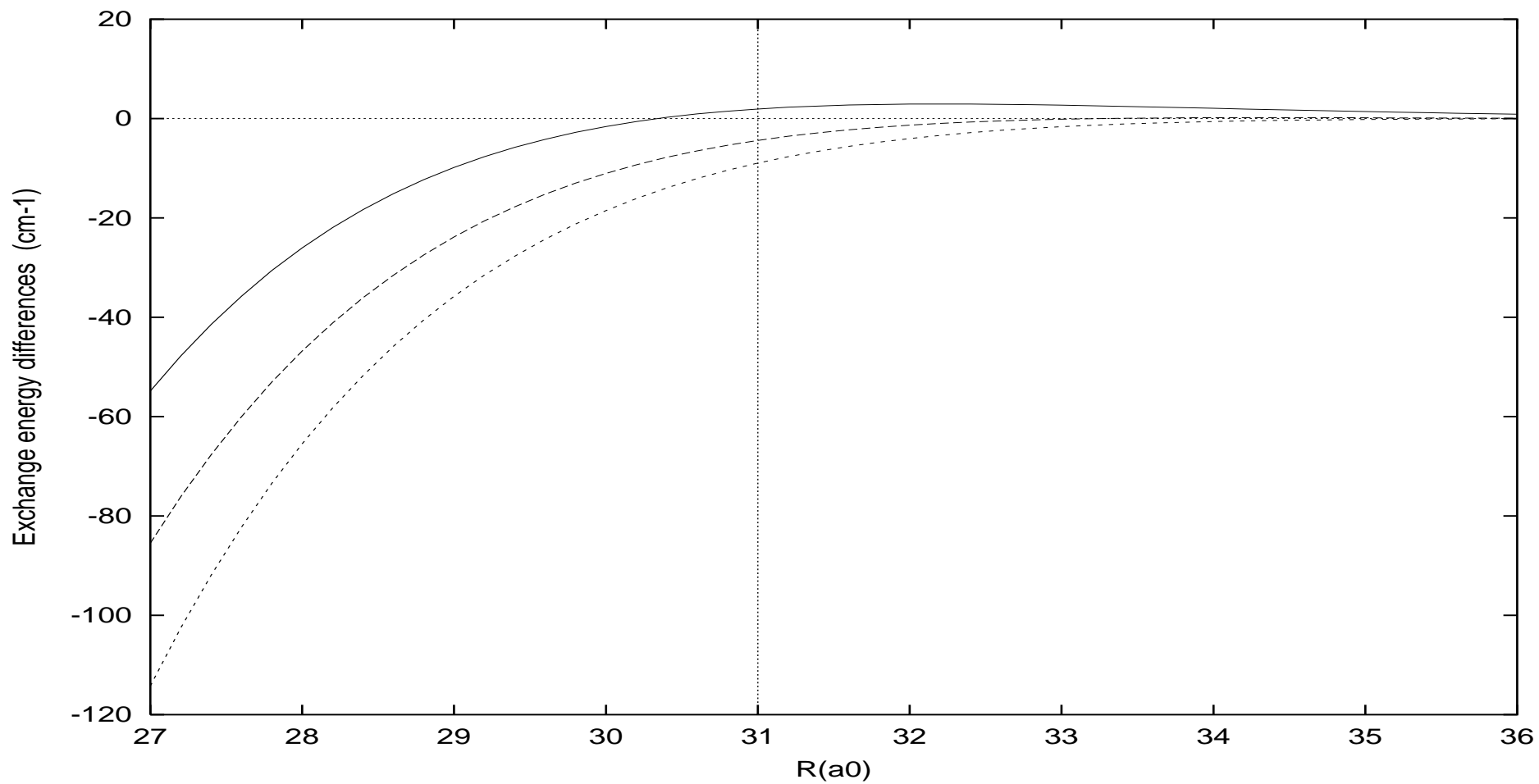


Figure 4: Differences between *ab initio* and long-range values of the exchange energy for the  $(2)^2\Sigma_u^+$  state of  $\text{Cs}_2^+$