

Calculation of exchange energies using algebraic perturbation theory

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An algebraic perturbation theory is presented for efficient calculations of localized states and hence of exchange energies, which are the differences between low-lying states of the valence electron of a molecule, formed by the collision of an ion Y^+ with an atom X . For the case of a homonuclear molecule these are the gerade and ungerade states and the exchange energy is an exponentially decreasing function of the internuclear distance. For such homonuclear systems the theory is used in conjunction with the Herring-Holstein technique to give accurate exchange energies for a range of intermolecular separations R . Since the perturbation parameter is essentially $1/R$, this method is suitable for large R . In particular, exchange energies are calculated for X_2^+ systems, where X is H, Li, Na, K, Rb, or Cs.

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I. INTRODUCTION

The problem of exchange energies between two low-lying states of a two-atom ionic system is considered. Initially, we examine the case where the atoms are hydrogenlike atoms separated by an internuclear distance R , which we then generalize to larger atoms, each with a predominant valence electron which is described in the same formalism. The solution of the nonrelativistic Schrödinger equation obtained is perturbative, based on the exact solutions at infinite separation; for the larger atoms, these are described by the asymptotic valence states determined by the ionization energies of the atoms. The perturbation can conveniently be described in an algebraic formalism but it follows the well-known technique of finding a perturbation expansion for the separation constant of the Schrödinger equation when spheroidal coordinates are used. The perturbation parameter is a function of both R and the energy E of the state considered, and E is determined by equating the expansions of the separation constant from each of the separated equations.

Initially, we concentrate on heteronuclear molecules but there has been much interest in the homonuclear systems [1–9], where the exchange energy is zero at infinite separation but, more significantly, decays exponentially with R . For sufficiently large R , it becomes impractical to merely subtract the energies of the two states considered. In addition, the preceding perturbation expansion is based on separate states at infinite separation, whereas in the homonuclear case the states are not localized on a particular atom for any value of R , however large. To overcome these problems, the Herring-Holstein result [7–9] is usually used, which expresses the exchange energy essentially as an integral over the median plane between the atoms together with a normalization term. This special case can be treated using the theory for heteronuclear systems by calculating ψ_A , the solution describing one of the atoms

perturbed by the other atom. In a later section of this article, exchange energies for several alkali-metal molecular ions are calculated for a large range of R .

II. HYDROGENLIKE HETERONUCLEAR SYSTEMS

The basic, *exact*, nonrelativistic Schrödinger equation for the interaction of two atoms is

$$\left(-\frac{1}{2}\nabla^2 - \frac{\mu_a}{r_a} - \frac{\mu_b}{r_b}\right)\Psi = E\Psi. \quad (1)$$

Here μ_a, μ_b are the charges on the atoms and the eigenvalue E is given by

$$E = W - \frac{\mu_a\mu_b}{R}, \quad (2)$$

where W is the exact energy. Equation (1) separates into spheroidal coordinates:

$$p = \frac{r_a + r_b}{R}, \quad q = \frac{r_a - r_b}{R}, \quad \Phi. \quad (3)$$

We consider here only those states for which the azimuthal quantum number is zero and write $\Psi = X(p)Y(q)$ to obtain

$$\frac{d}{dp} \left\{ (p^2 - 1) \frac{dX}{dp} \right\} + [-C - \lambda^2(p^2 - 1) + R(\mu_a + \mu_b)p]X = 0, \quad (4)$$

$$\frac{d}{dq} \left\{ (1 - q^2) \frac{dY}{dq} \right\} + [C - \lambda^2(1 - q^2) - R(\mu_a - \mu_b)q]Y = 0 \quad (5)$$

for $1 \leq p < \infty$, $-1 \leq q \leq 1$, where C is the separation constant and

$$\lambda = R\sqrt{-\frac{E}{2}}. \quad (6)$$

Equations (4) and (5) have the same essential form and may be treated analogously using transformations similar to those in [10,11]. In Eq. (4) we may use $x = 2\lambda(p - 1)$ and define $S = R(\mu_a + \mu_b)/\lambda$ so that, *asymptotically*, S is independent

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of R (it depends on R through the dependence of E on R). This leads to

$$\left(x + \frac{x^2}{4\lambda}\right) \frac{d^2 X}{dx^2} + \left(1 + \frac{x}{2\lambda}\right) \frac{dX}{dx} + \left(-\frac{C}{4\lambda} - \frac{x}{4} - \frac{x^2}{16\lambda} + \frac{S}{4} + \frac{Sx}{8\lambda}\right) X = 0. \quad (7)$$

Writing $X = \exp(-x/2)\phi = \exp[\lambda(p-1)]\phi$, we may rearrange Eq. (7) into a form suitable for perturbation theory:

$$\begin{aligned} L(\gamma, 1, x)\phi &= -\omega x L(s, 2, x)\phi, \\ L(a, b, x) &= xD^2 + (b-x)D - a, \end{aligned} \quad (8)$$

where

$$D = \frac{d}{dx}, \quad \omega = \frac{1}{4\lambda}, \quad \gamma = \omega C - \frac{S}{4} + \frac{1}{2}, \quad s = 1 - \frac{S}{2}, \quad (9)$$

so that $\omega \sim 1/R$ is a natural parameter for perturbation theory.

Asymptotically, we may neglect the right-hand side of Eq. (8) and obtain *exact* solutions to the resulting confluent hypergeometric equation. Only the regular Kummer M solution, $M(\gamma, 1, x)$, need be considered, since we require solutions which are regular at $x = 0$. To ensure a physical solution also as $x \rightarrow \infty$, we require $\gamma = -n$, where n is zero or a positive integer, leading to un-normalized solutions of the form

$$\phi = M(\gamma, 1, x). \quad (10)$$

For the ground state, $\gamma = n = 0$, and Eqs. (8) and (9) then yield

$$\phi_0 = 1, \quad \frac{C}{4\lambda} = \left(\frac{S}{4} - \frac{1}{2}\right). \quad (11)$$

To improve these results, we now expand ϕ and C in power series in ω , and use algebraic perturbation theory (PT). We introduce a standard realization of the generators of the $SO(2,1)$ Lie algebra,

$$J_- = xD^2 + D, \quad J_0 = xD + \frac{1}{2}, \quad J_+ = x, \quad (12)$$

which satisfy the usual commutation relationships

$$[J_0, J_+] = J_+, \quad [J_0, J_-] = -J_-, \quad [J_+, J_-] = -2J_0, \quad (13)$$

so that Eq. (8) becomes

$$\begin{aligned} [J_- - J_0 - (\gamma - \frac{1}{2})]\phi \\ = -\omega\{J_0 - \frac{1}{2} + J_+[J_- - J_0 + \frac{1}{2} - s]\}\phi. \end{aligned} \quad (14)$$

We first apply a similarity transformation (often called a ‘‘rotation’’ [12,13]) to Eq. (14) so that, for a general operator A ,

$$A\phi = 0 \rightarrow B\psi = 0, \quad (15)$$

where (B, ψ) are transforms of (A, ϕ) defined by

$$B = \hat{U}A\hat{U}^{-1}, \quad \psi = \hat{U}\phi. \quad (16)$$

With the particular choice

$$\hat{U} = \exp(J_-), \quad (17)$$

we have

$$J_0 \rightarrow J_0 + J_-, \quad J_+ \rightarrow (J_+ + 2J_0 + J_-), \quad (18)$$

and the *complete* Eq. (8) is transformed by Eqs. (16) and (17) to

$$h\psi = (h_0 + \omega h_1)\psi = \gamma\psi, \quad (19)$$

where

$$\begin{aligned} h_0 &= \left(\frac{1}{2} - J_0\right), \\ h_1 &= (J_+ + 2J_0 + J_-)(b + h_0) + (J_- - h_0), \\ b &= \frac{S}{2} - 1, \end{aligned} \quad (20)$$

and we now expand (ψ, γ) in a power series in ω . Since $\psi_0 = \hat{U}\phi_0$ for the correct behavior at infinite separation, we can proceed by ordinary PT, constructing the matrices for the J operators in the basis $\{x^n, n = 0, 1, 2, \dots\}$ so that n is a non-negative integer and arrive at the following matrix form of Eq. (19):

$$H_0\mathbf{x} = (\gamma - \omega H_1)\mathbf{x}. \quad (21)$$

We give a simple example of the matrix formulation in Appendix A.

If we now expand γ and the vector \mathbf{x} in powers of ω , we obtain for the ground state a conventional perturbation scheme beginning with $\gamma_0 = 0$ and $\mathbf{x}_0^T = (1, 0, 0, 0, \dots)$ corresponding to the asymptotic (zero-order) solution. The higher equations may be made consistent order by order through appropriate choices of the successive γ_n . These are polynomials in b and consequently functions of λ and hence of E . This is an elementary, but tedious, calculation, but which can be carried out quickly and straightforwardly using a standard symbolic mathematical package; here we have used MAPLE. Further details and an example of the operators involved and some of the polynomials obtained are given in Appendix A. We note that since J_{\pm} merely connect a basis element with an adjacent element, H_1 has a band structure whereby in the perturbation calculation, one new basis element is introduced at each order of perturbation.

Equation (5) can be treated analogously, choosing either $y = 2\lambda(1+q)$ appropriate for a function centered (localized) on atom A or $2\lambda(1-q)$ for localization on atom B at infinite separation. In either case, the algebraic treatment is based on the realization of the $SO(2,1)$ generators (dependent on y and $D = d/dy$ instead of x and $D = d/dx$) but is completely analogous to the preceding analysis. Here the appropriate basis consists of integral powers of y . We note that the terms in C in Eqs. (4) and (5) are of opposite sign, as a result of which the *sign* of ω is reversed in the analog of Eq. (8):

$$L(\delta, 1, y)\psi = \omega y L(t, 2, y), \quad (22)$$

where now

$$D = \frac{d}{dy}, \quad \delta = -\omega C + \frac{t}{2}, \quad t = 1 - \frac{T}{2}, \quad T = \frac{R(\mu_a - \mu_b)}{\lambda}. \quad (23)$$

TABLE I. Energies for the $1s\sigma$ state in HeH^{2+} using n th-order perturbation theory (PT n) (a.u.).

R	PT2	PT3	PT4	Exact
3	-1.6661	-1.6675	-1.6681	-1.6688
4	-1.7497	-1.7503	-1.7505	-1.7506
5	-1.7998	-1.8001	-1.8002	-1.8002
6	-1.8332	-1.8334	-1.8334	
8	-1.8750	-1.8750	-1.8750	
10	-1.9000	-1.9000	-1.9000	
50	-1.9800	-1.9800	-1.9800	

The two perturbation expansions calculated through m th order for the separation constant C depend finally only on λ , so that for any given (finite) R , we need to solve the equation

$$\sum_{j=0}^m \gamma^j \omega^j = \sum_{j=0}^m \delta^j (-\omega)^j \quad (24)$$

to obtain estimates of E . In each case the basis needs to be truncated, but we can ensure that it is sufficiently large not to affect the perturbation expansion since the zero-order function is 1 and the band structure of the matrices is such that only one extra basis function is needed for each order of perturbation. Thus, for m th-order perturbation the size of the matrices required is $m + 1$ and the calculations involved are essentially matrix multiplications together with the solution of the transcendental equation (24).

To examine this technique, we consider HeH^{2+} ($\mu_a = 2$, $\mu_b = 1$), for which we have comparison data for values of R from 3...5 [14,15], and the exchange energy at infinite separation is -1.5 . The two states considered are the $1s\sigma$ and $2p\sigma$ states, and it is well known that perturbation expansions for the latter are troublesome since it has the same energy at infinite separation as the $2s\sigma$ and $3d\sigma$ states. The results are given in Tables I and II (in atomic units).

The results for the $1s\sigma$ state are excellent even for low values of R , but for the $2p\sigma$ state they are less good for the smaller values of R . The form of H_1 in Eq. (17) is dominated by the matrix $J_{-}h_0$ and the maximum size of the elements increases as the order of the perturbation increases so that there are ranges of ω for which we have convergence and ranges where the perturbation expansion is asymptotic; for $R \approx 3$, in the case of $2p\sigma$, the perturbation is large, so an asymptotic expansion is likely. In the perturbation calculations in this article, we have chosen the higher-order perturbed vectors, \mathbf{x}_n , to have a zero component in \mathbf{x}_0 . This is not strictly necessary

TABLE II. Energies for the $2p\sigma$ state in HeH^{2+} using PT n (a.u.).

R	PT2	PT3	PT4	Exact
3	-0.4736	-0.5045	-0.5279	-0.5126
4	-0.4847	-0.5012	-0.5114	-0.5315
5	-0.4903	-0.5003	-0.5056	-0.5225
6	-0.4934	-0.5000	-0.5030	
8	-0.4966	-0.5000	-0.5011	
10	-0.4980	-0.5000	-0.5005	
50	-0.5000	-0.5000	-0.5000	

and there are free parameters in the PT. We hope to return to this problem in future work using the free parameters to improve the convergence properties of the perturbation calculation. One possibility for HeH^{2+} is to ensure orthogonality between the $1s\sigma$ and $2p\sigma$ states to all orders. However, the technique here was designed for large R , and for these larger values the lower-order perturbation results give consistent estimates.

III. GENERAL HETERONUCLEAR SYSTEMS

For these systems we have the Schrödinger equation

$$\left[-\frac{1}{2}\nabla^2 + V_A(r_a) + V_B(r_b) - \frac{1}{r_a} - \frac{1}{r_b} \right] \Psi = E\Psi, \quad (25)$$

where V_A and V_B are core potentials which die away fairly rapidly so that the system may be treated in the same way essentially in a region well away from either atom (where both V_A and V_B can be ignored) with $\mu_a = \mu_b = 1$, but the solution at infinite separation is different and needs closer analysis. We consider a state localized on atom A in a region where $V_A \approx V_B \approx 0$ and with a large internuclear separation so that $1/r_b$ may be replaced by $1/R$. We have a zero-order equation of the form

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a} \right) \Psi_a = E_a \Psi_a, \quad (26)$$

with E_a approximately equal to the ionization energy of the valence electron on atom A . For fixed $E_a = -\beta^2/2$ a solution of this hydrogenlike system, which vanishes as $r_a \rightarrow \infty$, may be written in the form

$$\Psi_a^0 = \exp(-\beta r_a) U(c, 2, 2\beta r_a) \sim \exp(-\beta r_a) (2\beta r_a)^{-c}, \quad (27)$$

$$c = 1 - \frac{1}{\beta},$$

where U denotes the Kummer U function. In the case where E_a is exactly equal to the ionization energy, this will be the required, spherically symmetric, solution at infinite separation. However, for large finite R , which corresponds to our zero-order situation, we have degenerate solutions of the equation in the form

$$\Psi_a^l = \exp(-\beta r_a) r_a^l P_l[\cos(\theta)] U(c + l, 2l + 2, 2\beta r_a) \sim (2\beta)^{-l} \Psi_a^0 P_l[\cos(\theta)] \quad (28)$$

and the required zero-order wave function is a linear combination of all of these solutions. This is examined in Appendix B, where it is shown that the spheroidal coordinates we are using are asymptotically equivalent to parabolic coordinates and using these coordinates we obtain for large R an appropriate one-centre wave function centered on atom A :

$$\Psi_a = \exp[-2R\alpha(p-1)] \exp[-2R\alpha(q+1)] \times U[d, 1, 2R\alpha(q+1)], \quad (29)$$

$$\alpha = \sqrt{-\frac{E_a}{2}}, \quad d = 1 - \frac{1}{2\alpha}.$$

A. Algebraic perturbation theory

The form of the asymptotic wave function is separable in p and q and of identical form in p to that for the hydrogenlike

systems. Thus, the analysis of Eq. (4) is unchanged. The asymptotic solution for Eq. (5) has an additional factor $U[d, 1, 2\lambda(q+1)]$, where

$$U(d, 1, y) = y^{-d} \left[1 - \frac{d^2}{y} + \frac{d^2(d+1)^2}{2!y^2} - \dots \right] = \exp(-J_-)y^{-d} \quad (30)$$

for large y . Thus, Eq. (5) can be analyzed analogously to the case of the hydrogenlike system and we have the algebraic perturbation equation,

$$h_0\psi = \omega((J_+ + 2J_0 + J_-)(b + h_0) + (J_- - h_0))\psi + \delta\psi, \quad (31)$$

where $T = 0$ so that $b = -1$. The required asymptotic solution of this equation is y^{-d} so that we may use the basis $\{y^{-d+n}\}$, where now n is any integer, positive or negative, and since

$$h_0y^{-d} = -dy^{-d}, \quad (32)$$

we have

$$\delta_0 = \frac{1}{2} - d. \quad (33)$$

Note that the negative values of n did not occur in the hydrogenlike heteronuclear systems since for these $J_-k = 0$ for any constant k , but in the general case this is no longer true. In all other respects the calculation is identical to the calculation for the hydrogenlike atoms and the band form of the perturbation matrices ensures that we only have two extra basis functions for each order of perturbation (one new positive value of n and one new negative value) and that consequently the basis can be truncated appropriately. In Tables III and IV the first-, second-, third-, and eighth-order perturbation results are presented for both Li and Na perturbed by $-\frac{1}{r_b}$ for a wide range of nuclear separations. Assuming R is sufficiently large so that in the region considered the core potentials are negligible and not affected by the other atom, then these solutions may be used as a model for the composite molecule Li-Na, and the exchange energies are obtained by subtracting the energies of the localized state. Thus, analogously to HeH^{2+} , we obtain two states localized on the different atoms. In homonuclear systems, and large R , subtracting two energies may not be a practical procedure and we need to examine the alternative approach using the Herring-Holstein theory.

TABLE III. Energies of perturbed Li using PT n (a.u.).

R	PT1	PT2	PT3	PT8
5	-0.19507	-0.22242	-0.23549	-0.25338
10	-0.19656	-0.20526	-0.20724	-0.20780
20	-0.19761	-0.20021	-0.20051	-0.20052
30	-0.19789	-0.19914	-0.19923	-0.19923
40	-0.19800	-0.19873	-0.19878	-0.19878
50	-0.19806	-0.19854	-0.19856	-0.19856
75	-0.19812	-0.19834	-0.19835	-0.19835
100	-0.19814	-0.19827	-0.19827	-0.19827
∞	-0.198174	-0.198174	-0.198174	-0.198174

TABLE IV. Energies of perturbed Na using PT n (a.u.).

R	PT1	PT2	PT3	PT8
5	-0.18756	-0.21540	-0.22826	-0.24618
10	-0.18821	-0.19709	-0.19907	-0.19963
20	-0.18905	-0.19171	-0.19202	-0.19204
30	-0.18930	-0.19057	-0.19067	-0.19068
40	-0.18940	-0.19015	-0.119019	-0.19019
50	-0.118944	-0.18994	-0.18996	-0.18996
75	-0.18950	-0.18973	-0.18973	-0.18974
100	-0.18952	-0.18965	-0.18966	-0.18966
∞	-0.189552	-0.189552	-0.189552	-0.189552

IV. THEORY OF HOMONUCLEAR HYDROGENLIKE SYSTEMS

The theory cannot be directly applied to homonuclear systems since for such systems, at infinite separation we do not have localization on one particular atom. The lowest states are the gerade and ungerade states, which are respectively symmetric and antisymmetric with respect to the median plane ($z = R/2$) between the two identical atoms. These two states, ψ_+ and ψ_- , can always be written in the form

$$\psi_+ = \frac{\psi_A + \psi_B}{\sqrt{2}}, \quad \psi_- = \frac{\psi_A - \psi_B}{\sqrt{2}}, \quad (34)$$

where ψ_A, ψ_B are states localized on atoms A and B , respectively. By symmetry considerations, on the median plane ψ_A, ψ_B satisfy

$$\psi_A = \psi_B, \quad \frac{\partial \psi_A}{\partial z} = -\frac{\partial \psi_B}{\partial z}, \quad (35)$$

and they can be obtained using the theory outlined previously, where one atom is perturbed by the other. In practice, using the symmetry, only one of the functions is required.

The exchange energy may be estimated from the Herring-Holstein theory, which is an application of Green's theorem for two states, which satisfy

$$\left(-\frac{1}{2}\nabla^2 + V\right)\psi_+ = E_+\psi_+, \quad \left(-\frac{1}{2}\nabla^2 + V\right)\psi_- = E_-\psi_-, \quad (36)$$

from which we may deduce

$$\begin{aligned} (E_+ - E_-) \int_{\hat{V}} \psi_+ \psi_- d\hat{V} &= -\frac{1}{2} \left[\int_{\hat{V}} (\psi_- \nabla^2 \psi_+ - \psi_+ \nabla^2 \psi_-) d\hat{V} \right] \\ &= \int_S \psi_A \nabla \psi_A \cdot \mathbf{k} dS, \end{aligned} \quad (37)$$

where S is the median plane and \hat{V} the spatial volume $z < R/2$. In terms of spheroidals, the median plane corresponds to $q = 0$ and

$$\nabla \cdot \mathbf{k} = \frac{2}{R} \frac{\partial}{\partial q}. \quad (38)$$

Thus the surface integral is

$$R\pi \int_{p=1}^{\infty} \psi_A \frac{\partial \psi_A}{\partial q} dp. \quad (39)$$

The volume integral may also be expressed in these coordinates and is

$$\left(\frac{R}{2}\right)^3 \pi \int_{q=-1}^{q=0} \int_{p=1}^{\infty} (\psi_A^2 - \psi_B^2)(p^2 - q^2) dp dq, \quad (40)$$

where ψ_B may be calculated from ψ_A , but it is more consistent to ignore ψ_B^2 in this interval since it is $O[\exp(-2R)]$ and terms of this order in ψ_A^2 cannot be obtained from our perturbation expansion, which is essentially in inverse powers of R . In order to examine these estimates, we have used the preceding theory to calculate the localized ψ_A for H-H at various values of R for which exact results are known. These are computed to eighth-order perturbation and used in a Herring-Holstein calculation for the exchange energies. These are given in Table V, where the well known Herring-Holstein asymptotic estimate is also given.

The perturbation results are universally better than the conventional asymptotic results. The calculation process, even for eighth-order perturbation, is fairly trivial since it only involves multiplication by matrices of low order. (In this latter calculation the basis was such that the matrices were of order 9×9 .) These matrix calculations are exact and the only numerical aspect is the solution of the transcendental equation (24) for the separation constant (the accuracy of this solution will clearly affect the accuracy of the results) and the truncation to the order of the perturbation used.

From these results we obtain an analytical expansion of the exchange energy in terms of R . To do this we first fit the parameter α of Eq. (29) to a set of the numerical results, obtaining

$$\alpha \approx 0.5 + \frac{0.5}{R} - \frac{0.2410}{R^2}. \quad (41)$$

TABLE V. Exchange energies for H_2^+ : Eighth-order perturbation theory (PT8) compared with the exact and asymptotic values (a.u.).

R	Asymptotic	PT8	Exact
4	0.107 8	0.093 91	0.100 5
6	0.021 88	0.021 40	0.021 36
7	0.009 39	0.009 33	0.009 32
8	0.003 95	0.003 96	0.003 99
9	0.001 634	0.001 648	0.001 652
10	0.000 668	0.000 676	0.000 677
11	0.000 270	0.000 274	0.000 275
12	0.000 108	0.000 110	0.000 114
13	4.32×10^{-5}	4.39×10^{-5}	4.40×10^{-5}
14	1.71×10^{-5}	1.74×10^{-5}	1.74×10^{-5}
15	6.76×10^{-6}	6.85×10^{-6}	6.88×10^{-6}
20	6.07×10^{-8}	6.15×10^{-8}	6.17×10^{-8}
30	4.13×10^{-12}	4.17×10^{-12}	4.19×10^{-12}

We used the values $R = 80$, $R = 90$, and $R = 100$ to obtain this expression. The analysis can then be done exactly using MAPLE and we obtain the exchange energy

$$\Delta E = R \left(3.984 39 + \frac{0.015 59}{R} - \frac{10.700 25}{R^2} - \frac{9.809 12}{R^3} \dots \right) \times \exp(-2\alpha R). \quad (42)$$

By analyzing the exponential terms, this may be expressed in the more conventional form:

$$\Delta E = R \exp(-R) \exp(-1) \times \left(1 + \frac{0.485 91}{R} - \frac{2.567 49}{R^2} - \frac{3.737 20}{R^3} \dots \right). \quad (43)$$

This is similar, but not identical, to the usual asymptotic expansion.

V. HOMONUCLEAR MOLECULES WITH CORE POTENTIALS

We may also consider the general homonuclear case by analyzing Eq. (25) when the atomic cores on atoms A and B are identical. We may apply the theory outlined previously given an approximation for d so that we can construct a basis. Taking E_a to be the ionization energy in Eq. (29) provides an appropriate basis and the localized perturbation calculation can be carried out from either atom. One important difference in the perturbation calculation is that at each order of the perturbation two extra basis functions are used (so that for the initial function y^{-d} , first-order PT would lead to contributions from the basis elements y^{-d+1}, y^{-d-1}). We may calculate (38) as in the H-H case since it depends only on the solution on the median plane, but we need to estimate the volume integral [Eq. (40)] from additional information about the atomic core. This is equivalent to finding a core-dependent normalization constant so that ψ_A may be replaced by $k\psi_a$.

A. Normalization

This problem has been considered in previous work [1,2,6] using perturbation based on radial coordinates and the zero-order wave function in the asymptotic region is taken to be Eq. (27) with E_a given by the ionization energy. There are many ways to estimate the normalization constant k [1,6] and all estimates seem to be consistent but using such a constant inevitably restricts the accuracy of the estimates of the exchange energies and leads to an uncertainty which may be estimated to be the order of 1%–3%. One way is to compute the value and derivative of Ψ_a^0 at some $r = r_0$ and solve for the total wave function numerically using pseudopotentials for the atomic cores [16], obtaining Ψ_a^0 for all r . The approximate zero-order wave function obtained is spherically symmetric, and this leads to simplification when the integration is carried out over a spherical region. In principle, this can be done for all Ψ_a^l . Since most of the contribution to Eq. (40) comes from the atomic core and a small asymptotic region, we may estimate the volume integral by integrating over a large spherical volume encompassing these regions. Over such a volume the wave function may be approximated by $\Psi_a^0 + \hat{\Psi}_a$,

TABLE VI. Exchange energies for Li_2^+ using PT8 (A) compared with variational calculations (B). In the rightmost column, the ratio between the two sets of numbers is given (a.u.).

R	A	B	Ratio
8	0.064 776 59	0.064 656 00	1.001 865 101
8.5	0.056 931 89	0.055 534 20	1.025 168 095
9	0.048 928 75	0.047 331 90	1.033 737 289
9.5	0.041 366 80	0.040 047 78	1.032 936 158
10	0.034 533 52	0.033 646 89	1.026 351 024
10.5	0.028 537 17	0.028 074 48	1.016 480 804
11	0.023 384 16	0.023 265 50	1.005 100 256
11.5	0.019 025 32	0.019 150 56	0.993 460 2435
12	0.015 383 94	0.015 659 38	0.982 410 2420
12.5	0.012 372 63	0.012 722 70	0.972 485 3785
13	0.009 903 39	0.010 273 50	0.963 974 3028
13.5	0.007 893 20	0.008 248 11	0.956 970 7484
14	0.006 266 90	0.006 586 68	0.951 450 5031
14.5	0.004 958 37	0.005 234 22	0.947 298 7379
15	0.003 910 60	0.004 141 05	0.944 349 2700
15.5	0.003 075 25	0.003 263 13	0.942 423 3788
16	0.002 411 85	0.002 562 14	0.941 342 0032
16.5	0.001 886 87	0.002 005 30	0.940 941 5050
17	0.001 472 75	0.001 564 97	0.941 072 3528
17.5	0.001 147 06	0.001 218 18	0.941 617 8233
18	0.000 891 60	0.000 946 03	0.942 464 8267
18.5	0.000 691 73	0.000 733 13	0.943 529 7969
19	0.000 535 72	0.000 567 05	0.944 749 1403
19.5	0.000 414 21	0.000 437 81	0.946 095 3382
20	0.000 319 76	0.000 337 48	0.947 493 1848
20.5	0.000 246 48	0.000 259 75	0.948 912 4158
21	0.000 189 73	0.000 199 64	0.950 360 6492
21.5	0.000 145 86	0.000 153 24	0.951 840 2506
22	0.000 111 98	0.000 117 48	0.953 183 5206
22.5	0.000 085 88	0.000 089 96	0.954 646 5096
23	0.000 065 78	0.000 068 81	0.955 965 707
23.5	0.000 050 33	0.000 052 58	0.957 208 0639
24	0.000 038 47	0.000 040 13	0.958 634 4381
24.5	0.000 029 38	0.000 030 60	0.960 130 7190
25	0.000 022 41	0.000 023 31	0.961 389 9614
25.5	0.000 017 08	0.000 017 74	0.962 795 9414
27	0.000 007 53	0.000 007 78	0.967 866 3239
26	0.000 013 01	0.000 013 49	0.964 418 0875
26.5	0.000 009 90	0.000 010 25	0.965 853 6585
27.5	0.000 005 72	0.000 005 90	0.969 491 5254
28	0.000 004 34	0.000 004 47	0.970 917 2260
28.5	0.000 003 29	0.000 003 38	0.973 372 7811
29	0.000 002 50	0.000 002 55	0.980 392 159
30	0.000 001 43	0.000 001 45	0.986 206 8966
31	$8.190333400 \times 10^{-7}$	$8.468815650 \times 10^{-7}$	0.967 116 7420
32	$4.675271850 \times 10^{-7}$	$4.829070270 \times 10^{-7}$	0.968 151 5465
33	$2.663025430 \times 10^{-7}$	$2.747848940 \times 10^{-7}$	0.969 130 9414
35	$8.588708750 \times 10^{-8}$	$8.845697500 \times 10^{-8}$	0.970 947 5991
37	$2.750188780 \times 10^{-8}$	$2.827647290 \times 10^{-8}$	0.972 606 7285
39	$8.750160620 \times 10^{-9}$	$8.982464200 \times 10^{-9}$	0.974 138 1012
40	$4.924821370 \times 10^{-9}$	$5.051807900 \times 10^{-9}$	0.974 863 1515

where $\hat{\Psi}_a$ is a combination of functions of the form given in Eq. (28) and these are orthogonal to Ψ_a^0 over this volume. Consequently, to lowest order, we may simply renormalize Ψ_a^0 so that the volume integral is unity. To use this, we need to

TABLE VII. Exchange energies for Li_2^+ using PT8 (A) compared with pseudopotential calculations (B) (a.u.).

R	A	B
20	3.20×10^{-4}	3.34×10^{-4}
30	1.43×10^{-6}	1.46×10^{-6}
40	4.92×10^{-9}	4.96×10^{-9}
50	1.47×10^{-11}	1.47×10^{-11}
60	4.02×10^{-14}	4.02×10^{-14}
70	1.04×10^{-16}	1.03×10^{-16}
80	2.55×10^{-19}	2.54×10^{-19}
90	6.06×10^{-22}	6.05×10^{-22}

normalize our solution in Eq. (29) in the same way as $R \rightarrow \infty$ and it suffices to ensure this using the z axis ($p = 1$) so that we need to choose

$$k = \frac{\hat{q}}{\sqrt{4\pi}} \frac{1}{(2\beta)^d}, \quad (44)$$

where \hat{q} is taken from the numerical calculation or from previous estimates. In order to compare with some previous calculations we have taken the values from [2] and these are given in Appendix C, together with the other parameters used for the ions Li_2^+ , Na_2^+ , K_2^+ , Rb_2^+ , and Cs_2^+ . In Table VI (A) with some variational calculations (B) [17] and note that there is good agreement. The variational calculations are more challenging for the larger values of R where current interest lies and in Table VII we compare our estimates for larger R with results obtained in [2]. Finally, in Table VIII we give our estimates for the exchange energies of the other systems. We note that in the earlier work of Bardsley *et al.* [1], the exchange energies were estimated using a two-term asymptotic expansion. Even though the parameters used were slightly different the results obtained are consistent with our values.

The results quoted are evaluated from analytical formulas obtained for the exchange energies, analogously to Eq. (42) for H_2^+ , rather than the slightly more accurate numerical results. As in the construction of Eq. (41) it is first necessary to fit α to a set of the energies and then we obtain a formula of the form

$$\Delta E = k(\alpha R)^{-2d} R \exp(-2\alpha R) \left(A + \frac{B}{R} + \frac{C}{R^2} \dots \right) \quad (45)$$

TABLE VIII. Exchange energies for Na_2^+ , K_2^+ , Rb_2^+ , and Cs_2^+ using PT8 analytically using a fit to α (a.u.).

R	Na-Na	K-K	Rb-Rb	Cs-Cs
10	4.03×10^{-2}	5.99×10^{-2}	6.73×10^{-2}	1.57×10^{-1}
15	5.04×10^{-3}	1.22×10^{-2}	1.48×10^{-2}	2.03×10^{-2}
20	4.50×10^{-4}	1.57×10^{-3}	2.08×10^{-3}	3.38×10^{-3}
30	2.38×10^{-6}	1.57×10^{-5}	2.40×10^{-5}	5.07×10^{-5}
40	9.60×10^{-9}	1.15×10^{-7}	1.99×10^{-7}	5.29×10^{-7}
50	3.35×10^{-11}	7.10×10^{-10}	1.39×10^{-9}	4.59×10^{-9}
60	1.07×10^{-13}	3.96×10^{-12}	8.75×10^{-12}	3.57×10^{-11}
70	3.18×10^{-16}	2.06×10^{-14}	5.12×10^{-14}	2.57×10^{-13}
80	9.10×10^{-19}	1.02×10^{-16}	2.84×10^{-16}	1.75×10^{-15}
90	2.51×10^{-21}	4.82×10^{-19}	1.51×10^{-18}	1.14×10^{-17}

by fitting at $R = 90$, $R = 100$, and $R = 500$. The values of A , B , and C and the expressions for α are given in Appendix C for all the systems considered. The perturbation series for Cs is beginning to behave as an asymptotic series for $R \approx 10 \dots 15$ and lower-order perturbation is preferable, but the fitted formula reproduces these lower-order estimates to 1% or 2%. The results obtained show that the algebraic approach provides an accurate method for estimating exchange energies for a wide range of systems. In the case of homonuclear molecules, we show that it can be applied to Li_2^+ , Na_2^+ , K_2^+ , Rb_2^+ , and Cs_2^+ and is not restricted to H_2^+ . Further work is in progress, particularly on the heteronuclear systems that have been less widely studied.

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APPENDIX A

If we employ a finite basis $\{x^n$ with $n = 0, 1, 2, 3\}$, then the matrices J_0 , J_+ , J_- , and H_1 are given by

$$J_0 = \begin{pmatrix} 0.5 & 0 & 0 & 0 \\ 0 & 1.5 & 0 & 0 \\ 0 & 0 & 2.5 & 0 \\ 0 & 0 & 0 & 3.5 \end{pmatrix}, \quad J_+ = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix},$$

$$J_- = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 4 & 0 \\ 0 & 0 & 0 & 9 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad (A1)$$

$$H_1 = \begin{pmatrix} b & b & 0 & 0 \\ b & 3b-2 & 4b-4 & 0 \\ 0 & b-1 & 5b-8 & 9b-18 \\ 0 & 0 & b-2 & 7b-18 \end{pmatrix}.$$

We use the generic form of the perturbation equation given in Sec. II for either the p or the q equation:

$$H_0 \mathbf{x} = (k - \hat{\omega} H_1) \mathbf{x}, \quad \mathbf{x}_0^T = (1, 0, 0, 0), \quad (A2)$$

with H_0 the matrix representation of h_0 and $\hat{\omega} = \pm\omega$, $k = \gamma, \delta$ depending on which of the p or q equations are used. The n th-order vector \mathbf{x}_n ($n \neq 0$) is chosen to have no component in \mathbf{x}_0 and the first-, second-, and third-order values of γ are given by the polynomials b , b^2 , and $2b^3 - 2b$, respectively. The definition of b differs for the p and q equations (see Sec. II).

In the more general case of the core potentials, the initial vector will be of the form $\mathbf{x}_0^T = (\dots, 0, 0, 0, 1, 0, 0, 0 \dots)$, depending on the number of basis elements used, and the polynomials will depend on d in addition to b .

APPENDIX B: COORDINATE SYSTEMS

We may use parabolic coordinates at one center (atom) so that

$$x = \sqrt{uv} \cos(\Phi), \quad y = \sqrt{uv} \sin(\Phi), \quad z = \frac{1}{2}(u - v). \quad (B1)$$

We are interested in an arbitrary plane so that for σ states, we may take $\Phi = 0$ and from atom A

$$r_a^2 = uv + \frac{1}{4}(u - v)^2 = \left(\frac{u + v}{2}\right)^2. \quad (B2)$$

Thus,

$$r_a = \frac{u + v}{2}, \quad z_a = r_a \cos(\theta_a) = \frac{1}{2}(u - v) \Rightarrow$$

$$u_a = r_a[1 + \cos(\theta_a)], \quad v_a = r_a[1 - \cos(\theta_a)]. \quad (B3)$$

This has made a direct connection between parabolic and radial, one-center coordinates and we now seek to connect them, asymptotically, to spheroidals where atom A is one of the foci. Since u_a, v_a are orthogonal coordinates, then so are

$$p = 1 + \frac{v_a}{R}, \quad q = -1 + \frac{u_a}{R}. \quad (B4)$$

Thus,

$$\left(1 + \frac{v_a}{R}\right) + \left(-1 + \frac{u_a}{R}\right) = \frac{2r_a}{R} = p + q, \quad (B5)$$

where p and q satisfy the same relationship as the spheroidal coordinates. Also,

$$\frac{R}{2}(pq + 1) = \frac{R}{2} \left(\frac{u_a - v_a}{R}\right) + O\left(\frac{1}{R}\right) \sim z_a \quad (B6)$$

as $R \rightarrow \infty$, which shows that p and q approach the relationships satisfied by the spheroidal coordinates asymptotically. The relationships are the same from atom B, except we take

$$p = 1 + \frac{v_b}{R}, \quad q = 1 - \frac{u_b}{R} \quad (B7)$$

and the z coordinate measured from B (in the direction of A) is such that

$$\frac{R}{2}(-pq + 1) = \frac{R}{2} \left(\frac{u_b - v_b}{R}\right) + O\left(\frac{1}{R}\right) \sim z_b. \quad (B8)$$

Thus, asymptotically, we have

$$p \approx 1 + \frac{v_a}{R} \approx 1 + \frac{v_b}{R}, \quad q \approx -1 + \frac{u_a}{R} \approx 1 - \frac{u_b}{R}. \quad (B9)$$

We now consider atom A at large separation so that the effect of atom B can be ignored, but where r_a is sufficiently large so that any core potential V_A may be neglected:

$$H_0 \Psi = \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_a}\right) \Psi = E_a \Psi. \quad (B10)$$

In parabolic coordinates we have

$$\nabla^2 = \frac{4}{u + v} \{L_u + L_v\}, \quad L_x = x D_x^2 + D_x, \quad D_x = \frac{d}{dx}, \quad (B11)$$

so that we have

$$\left[L_u + L_v + 1 + \frac{E_a(u+v)}{2} \right] F_0(u)G_0(v) = 0, \quad \Psi = F_0G_0. \quad (\text{B12})$$

We may separate this equation in a variety of ways, and a separation convenient for our analysis is

$$\left(L_u + \frac{E_a}{2}u + 1 \right) F_0 = kF_0, \quad (\text{B13})$$

$$\left(L_v + \frac{E_a}{2}v \right) G_0 = -kG_0. \quad (\text{B14})$$

In Eq. (B14) we may write $G_0 = \exp(-\alpha v)g_0$, with $2\alpha^2 = -E_a$ and obtain the equation for g_0 :

$$[vD_v^2 + (1 - 2\alpha v)D_v + k - \alpha]g_0 = 0. \quad (\text{B15})$$

Substituting $s = 2\alpha v$ gives

$$[sD_s^2 + (1 - s)D_s - c]g_0 = 0, \quad c = \frac{1}{2} - \frac{k}{2\alpha}. \quad (\text{B16})$$

This is a Kummer equation and since we require g_0 to be finite as $s \rightarrow 0$ we need to use the Kummer M function and

$$g_0 = M(c, 1, 2\alpha v). \quad (\text{B17})$$

However, we also require the solution to be finite as $v \rightarrow \infty$ then the function must truncate to a polynomial; for the ground state, this implies that

$$c = 0 \Rightarrow k = \alpha. \quad (\text{B18})$$

With this value of k we may use $F_0 = \exp(-\alpha u)f_0$ in Eq. (B12) to obtain

$$[uD_u^2 + (1 - 2\alpha u)D_u + 1 - 2\alpha]f_0 = 0. \quad (\text{B19})$$

Putting $s = 2\alpha u$ gives the Kummer equation

$$[sD_s^2 + (1 - s)D_s - d]f_0 = 0, \quad d = 1 - \frac{1}{2\alpha}. \quad (\text{B20})$$

In the region considered where u is large (and well away from the origin) and d is fixed, we require to use of the Kummer U function to ensure the correct behavior for large $u \leq R$ so that we have

$$f_0 = U(d, 1, 2\alpha u). \quad (\text{B21})$$

[In the case of the ground state of hydrogenlike atoms, we have $d = 0$, but in that case $U(0, 1, 2\alpha u) = M(0, 1, 2\alpha u) = 1$ and the analysis is then identical with the analysis of this case.]

Thus, we have found the complete one-center wave function from A at large separation for a fixed E_a and we have an approximate zero-order function for our perturbation procedure,

$$\psi_a \approx \exp[-\alpha(u_a + v_a)]U(d, 1, 2\alpha u_a) \sim \exp[-\lambda(p - 1)] \times \exp[-\lambda(q + 1)]U(d, 1, 2\lambda(q + 1)), \quad (\text{B22})$$

where $\lambda = R\sqrt{-E_a/2}$ and E_a approaches the ionization energy for atom A as $R \rightarrow \infty$.

APPENDIX C

1. For Li we use $d = 0.588\,406\,5$, $\hat{q} = 0.814\,596$, $A = 2$, $B = -3.888\,34$, $C = -25.964\,65$, and the expansion for α is

$$0.314\,807\,101 + \frac{0.794\,320\,15}{R} - \frac{0.223\,527\,154}{R^2}.$$

2. For Na we use $d = 0.624\,130$, $\hat{q} = 0.675\,12$, $A = 2$, $B = -4.300\,44$, $C = -23.723\,33$, and the expansion for α is

$$0.307\,856\,900 + \frac{0.812\,212\,6}{R} - \frac{0.225\,614\,003}{R^2}.$$

3. For K we use $d = 0.770\,436$, $\hat{q} = 0.598\,446$, $A = 2$, $B = -6.240\,31$, $C = -36.012\,88$, and the expansion for α is

$$0.282\,415\,606 + \frac{0.885\,737\,2}{R} - \frac{0.336\,696\,40}{R^2}.$$

4. For Rb we use $d = 0.804\,772$, $\hat{q} = 0.569\,227$, $A = 2$, $B = -6.75\,747$, $C = -36.695\,09$, and the expansion for α is

$$0.277\,042\,0918 + \frac{0.903\,225\,9}{R} - \frac{0.434\,595\,52}{R^2}.$$

5. For Cs we use $d = 0.869\,254$, $\hat{q} = 0.509\,376$, $A = 2$, $B = -7.795\,47$, $C = -46.171\,54$, and the expansion for α is

$$0.267\,481\,791 + \frac{0.937\,757\,759\,17}{R} - \frac{0.968\,095\,334\,45}{R^2}.$$

The parameters \hat{q} and d are obtained from the explicit core potentials in [16].

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