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FIXED NUCLEI TWO-CENTRE PROBLEM IN QUANTUM MECHANICS†

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CONTENTS

A special non-crossing rule for the potential curves of one-electron diatomic molecules is proved and then used to correlate united atom and separated atom states. A new technique for finding the asymptotic expansion of the electronic energy W in inverse powers of the internuclear distance R is developed and the expansion of W is found through $O(1/R^6)$, with the coefficients expressed in terms of the nuclear charges and separated atom quantum numbers. Exponentially small corrections to the asymptotic expansion are evaluated and the g–u homonuclear and quasi-crossing heteronuclear energy splittings are discussed.

Introduction

One-electron diatomic molecules (o.e.d.ms) are the simplest of all molecular systems; as such, they constitute an important problem in quantum mechanics. Neglecting the nuclear motion, the Schrödinger equation for a general o.e.d.m. with nuclear charges Z_a and Z_b and internuclear distance R is (in atomic units, $m = e = \hbar = 1$)

$$(\tfrac{1}{2}\nabla^2 + Z_a/r_a + Z_b/r_b + W)\,\Psi(\boldsymbol{r};\, R) = 0, \tag{1}$$

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where $W = W(R) = E(R) - Z_a Z_b/R$ is the electronic energy. The classical analogue of (1) is separable in confocal spheroidal (elliptic) coordinates (Pauli 1922),

$$\left.\begin{array}{lll} \xi = (r_a + r_b)/R, & \eta = (r_a - r_b)/R, & \phi = \text{azimuthal angle} \\ 1 \leqslant \xi \leqslant \infty & -1 \leqslant \eta \leqslant 1 & 0 \leqslant \phi \leqslant 2\pi \end{array}\right\}, \tag{2}$$

where r_a and r_b are the distances of the electron from nuclei a and b, and hence (1) is also separable in these coordinates (Burrau 1927).

We assume that

$$\Psi(\boldsymbol{r}; R) = X(\xi)\, Y(\eta) \exp(\pm im\phi), \tag{3}$$

where $m = 0, 1, 2, \ldots$ is the modulus of the magnetic quantum number, and obtain the well-known 'inner' and 'outer' equations:

$$\frac{\mathrm{d}}{\mathrm{d}\eta}(1-\eta^2)\frac{\mathrm{d}Y}{\mathrm{d}\eta} + \left(C - p^2(1-\eta^2) - \frac{m^2}{1-\eta^2} - R(Z_a - Z_b)\,\eta\right) Y = 0, \tag{4}$$

$$\frac{\mathrm{d}}{\mathrm{d}\xi}(\xi^2-1)\frac{\mathrm{d}X}{\mathrm{d}\xi} + \left(-C - p^2(\xi^2-1) - \frac{m^2}{\xi^2-1} + R(Z_a + Z_b)\,\xi\right) X = 0. \tag{5}$$

C is the separation constant, and

$$p = R(-\tfrac{1}{2}W)^{\frac{1}{2}} \tag{6}$$

(we only consider $W < 0$). Subject to the usual conditions that the wavefunctions be square integrable, continuous, and have continuous first derivatives, simultaneous solutions of the coupled system of Sturm–Liouville equations (4) and (5) exist for only a discrete (denumerably infinite) set of pairs of eigenparameters p and C.

In the two limits $R \to 0$ and $R \to \infty$, we can give simple closed formulae for the energies and wavefunctions of o.e.d.ms. For R very large (or small), an asymptotic expansion of W in powers of $1/R$ (or R) is known. However, in general, we must resort to numerical solutions of these equations. Extensive tables of eigenparameters have been compiled by Bates, Ledsham & Stewart (1953), Wallis & Hulbert (1954), Peek (1965), Bates & Reid (1968) and Madsen & Peek (1971) for H_2^+, by Bates & Carson (1956) for HeH^{2+}, and by Ponomarev & Puzynina (1966, 1970) for $Z_a = 1$ to 8, $Z_b = 1$.†

In the first section of this paper, I prove a special o.e.d.m. non-crossing rule and use it to correlate the united atom (u.a.) and separated atom (s.a.) states. Next, I show how the general formula for the large R asymptotic expansion of W in powers of $1/R$ can be obtained by using only simple algebraic operations which are readily adapted for computer evaluation, and extend the expansion through $O(1/R^6)$. I conclude with a discussion of the exponentially small corrections to the $1/R$ expansion, and of the quasi-crossings of potential curves.

United atom limit

As $R \to 0$,

$$R\xi \to 2r, \quad \eta \to \cos\theta, \quad \phi \text{ is unchanged}, \tag{7}$$

where (r, θ, ϕ) are the usual spherical coordinates (I am using right-handed coordinate systems on both centres, with the positive z-axis directed from a to b). In terms of the u.a. charge

$$Z = Z_a + Z_b$$

† I have recently developed a computer program, to be described in a subsequent paper, with which one can quickly and inexpensively duplicate all of the results tabulated in these papers.

and quantum numbers $n = 1, 2, \ldots$; $l = 0, 1, \ldots, n-1$; and $m = 0, 1, \ldots, l$, we have

$$W_{nlm}(0) = -Z^2/2n^2, \tag{8}$$

$$\Psi_{nlm}(\mathbf{r}; 0) = A_{nlm} r^l L^{2l+1}_{n-l-1}(2Zr/n) \exp(-Zr/n)\, P^m_l(\cos\theta) \exp(\pm im\phi), \tag{9}$$

where A_{nlm} is the normalization constant, and I am adopting the definitions of Abramowitz & Stegun (1964) for the associated Laguerre and Legendre polynomials. In view of (7), at $R = 0$ the inner equation must become the differential equation for associated Legendre polynomials, and the outer equation the familiar radial equation for one-electron atoms. Equating eigenparameters, we get

$$p/R \to Z/2n, \quad C \to l(l+1). \tag{10}$$

Ignoring normalization, as $R \to 0$,

$$X(\xi) \to (p\xi)^l L^{2l+1}_{n-l-1}(2p\xi) \exp(-p\xi), \tag{11}$$

$$Y(\eta) \to P^m_l(\eta). \tag{12}$$

Following Hund (1928), the states of general o.e.d.ms are customarily labelled according to their u.a. limit quantum numbers as $n\{l\}\{m\}$, where

$$\left.\begin{aligned} \{l\} &= \text{s, p, d, f, g, } \ldots \text{ (skip j) } \ldots \quad \text{for} \quad l = 0, 1, 2, \ldots, \\ \{m\} &= \sigma, \pi, \delta, \varphi, \ldots \quad \text{for} \quad m = 0, 1, 2, \ldots. \end{aligned}\right\} \tag{13}$$

For homonuclear o.e.d.ms a subscript $_g$ or $_u$ describing the inversion symmetry is appended, $_g$ for l even, $_u$ for l odd.

Separated atom limit

As $R \to \infty$, the elliptic coordinates ξ and η become parabolic coordinates,

$$\left.\begin{aligned} \xi &\to 1 + \lambda_a/R \simeq 1 + \lambda_b/R, \\ \eta &\to -1 + \mu_a/R \simeq 1 - \mu_b/R, \end{aligned}\right\} \tag{14}$$

where, in terms of (right-handed) spherical coordinates on each centre,

$$\left.\begin{aligned} \lambda_a &= r_a(1 - \cos\theta_a), \quad \lambda_b = r_b(1 + \cos\theta_b), \\ \mu_a &= r_a(1 + \cos\theta_a), \quad \mu_b = r_b(1 - \cos\theta_b). \end{aligned}\right\} \tag{15}$$

In terms of parabolic coordinates, an (unnormalized) atomic eigenfunction on centre a is of the form (Morse & Stueckelberg 1929)

$$L^m_{K_a}(\zeta_a\mu_a)\, L^m_{N_a-K_a-m-1}(\zeta_a\lambda_a)\, (\mu_a\lambda_a)^{\frac{1}{2}m} \exp(-\tfrac{1}{2}\zeta_a(\mu_a + \lambda_a) \pm im\phi), \tag{16}$$

where $N_a = K_a + m + 1, K_a + m + 2, \ldots$ is the s.a. total quantum number, $K_a = 0, 1, \ldots$, is the parabolic quantum number, and $\zeta_a = Z_a/N_a$. The s.a. energy is

$$W_{N_a K_a m}(\infty) = -\tfrac{1}{2}\zeta_a^2 = -\tfrac{1}{2}Z_a^2/N_a^2. \tag{17}$$

For a o.e.d.m. state for which the electron is localized on centre a as $R \to \infty$, we thus expect that

$$\begin{aligned} \Psi^a_{N_a K_a m}(\mathbf{r}; R) = {} & ((\xi-1)(1+\eta))^{\frac{1}{2}m} \exp(\pm im\phi) \\ & \times L^m_{K_a}(\zeta_a R(1+\eta)) L^m_{N_a-K_a-m-1}(\zeta_a R(\xi-1)) \exp(-\tfrac{1}{2}\zeta_a R(\xi+\eta)) \end{aligned} \tag{18}$$

will be a good approximation to Ψ for R large, becoming exact for R infinite. When no confusion can arise, we will drop the subscript $_a$ from the parameters. We have analogous expressions for centre b, with $_a$ replaced by $_b$ in (16) to (18) and η by $-\eta$ in (18).

In the homonuclear case, we cannot distinguish between Ψ^{a}_{NKm} and Ψ^{b}_{NKm}, and therefore must express the o.e.d.m. wavefunction as a linear combination of these two atomic functions (Morse & Stueckelberg),

$$\Psi = \Psi^{\mathrm{a}}_{NKm} \pm \Psi^{\mathrm{b}}_{NKm} \tag{19}$$

$$= \exp(\pm \mathrm{i}m\phi)\, L^m_{N-K-m-1}(\zeta R(\xi-1))\,(\xi-1)^{\frac{1}{2}m} \exp(-\tfrac{1}{2}\zeta R\xi) \times \{(1+\eta)^{\frac{1}{2}m} L^m_{K_{\mathrm{b}}}(\zeta R(1+\eta)) \exp(-\tfrac{1}{2}\zeta R\eta) \pm (1-\eta)^{\frac{1}{2}m} L^m_K(\zeta R(1-\eta)) \exp(\tfrac{1}{2}\zeta R\eta)\}. \tag{20}$$

Ψ^{a} and Ψ^{b} have equal weights in (19) by symmetry.

In the heteronuclear case, if

$$Z_{\mathrm{a}}/N_{\mathrm{a}} = Z_{\mathrm{b}}/N_{\mathrm{b}}, \tag{21}$$

then $\Psi^{\mathrm{a}}_{N_{\mathrm{a}}K_{\mathrm{a}}m}$ and $\Psi^{\mathrm{b}}_{N_{\mathrm{b}}K_{\mathrm{b}}m}$ are degenerate at $R = \infty$. If we choose K_{a} and K_{b} so that

$$N_{\mathrm{a}} - K_{\mathrm{a}} - m - 1 = N_{\mathrm{b}} - K_{\mathrm{b}} - m - 1, \tag{22}$$

these two functions will have the same $X(\xi)$, and any arbitrary linear combination of them is of the required product form, (3). Do we need to allow for generalizations of the homonuclear form, (19), in cases such as this? Consider the one-centre s.a. state (18) perturbed by a point charge of magnitude Z_{b} at a large distance R along the z-axis. Neglecting terms that die off exponentially in R, a simple perturbation calculation of the energy through first-order gives

$$W(R) = -Z^2_{\mathrm{a}}/2N^2_{\mathrm{a}} - Z_{\mathrm{b}}/R + O(1/R^2). \tag{23}$$

For R large but finite, the energies of the two states under consideration differ by

$$(Z_{\mathrm{a}} - Z_{\mathrm{b}})/R + O(1/R^2).$$

They are degenerate only when R is infinite. However, with R infinite, all matrix elements between Ψ^{a} and Ψ^{b} are zero, and they do not interact. We thus conclude that as $R \to \infty$, the wavefunction for a heteronuclear o.e.d.m. will assume the one-centre form of either Ψ^{a} or Ψ^{b}.

Quantum numbers and nodes

A real function $f(x)$, with range $\alpha \leqslant x \leqslant \beta$, is said to have a node at $x = \gamma$ if $f(\gamma) = 0$, $f'(\gamma) = \mathrm{d}f/\mathrm{d}x|_{x=\gamma} \neq 0$, and γ is not equal to α or β. Note that having $f'(\gamma) \neq 0$ guarantees that $f(x)$ will change sign as x passes through γ, and rules out cases such as $f(x) = 0$ or $f(x) = (x-\gamma)^2$ being classified as nodes. We shall always choose $X(\xi)$ and $Y(\eta)$ to be real functions. Instead of the complex $\exp(\pm \mathrm{i}m\phi)$ we can use the linearly independent real functions $\cos m\phi$ and $\sin m\phi$ in discussing nodes for ϕ.

Let the number of nodes in each coordinate be specified by the nodal quantum numbers n_ξ, n_η, and n_ϕ. Since $L^k_j(x)$, $P^k_{j+k}(x)$, and $\cos jx$ or $\sin jx$ each have j nodes in their appropriate range of x (we count the cyclic pairs, such as $\cos\frac{1}{2}\pi$ and $\cos\frac{3}{2}\pi$, as only one node), we can establish a correspondence between the u.a. and s.a. quantum numbers and the nodal quantum numbers. Using (11) and (12), we have for the united atom

$$n_\xi = n - l - 1, \quad n_\eta = l - m, \quad n_\phi = m. \tag{24}$$

For the separated atom limit of a homonuclear o.e.d.m., the term in (20) with factor $\exp(-\frac{1}{2}\zeta R\eta)$ contributes K nodes in $Y(\eta)$ for $\eta < 0$, the other term K nodes for $\eta > 0$, and we get one more node, at $\eta = 0$, if the minus sign is used. Thus,

$$n_\xi = N - K - m - 1, \quad n_\phi = m, \quad n_\eta = \text{either} \begin{Bmatrix} 2K \\ 2K+1 \end{Bmatrix}. \tag{25}$$

For the s.a. states of a heteronuclear o.e.d.m. which dissociates with the electron localized on centre a, we have from (18)

$$n_\xi = N_a - K_a - m - 1, \quad n_\eta = K_a, \quad n_\phi = m. \tag{26}$$

The outer equation, (5), is invariant to interchanging the nuclei, but, when $Z_a \neq Z_b$, the inner equation is not invariant to this interchange. Any asymmetry in the charge distribution along the molecular axis when $Z_a \neq Z_b$ must be given by $Y(\eta)$. When R is large and the electron dissociates on centre a, the average value of $Y(\eta)$ for η near $+1$ will be much smaller than that for η near -1. The assignment $n_\eta = K_a$ in (26) ignores any nodes in $Y(\eta)$ near centre b; if there are nodes in $Y(\eta)$ for η near $+1$ with R large but finite, then (26) will be correct only when R is infinite. Nevertheless, for a s.a. state on centre a, this is the correct value of n_η to use in the forthcoming expansion of W in powers of $1/R$.

Dissociation products: are nodes conserved?

It is very useful to establish a one-to-one correspondence between the u.a. and s.a. states of a general o.e.d.m. One can draw many useful qualitative conclusions from this correlation, such as the general form and required crossings of the potential curves.

Given this problem, quite likely ones first inclination would be to try to use the von Neumann–Wigner non-crossing rule† (which states that potential curves of states of the same symmetries cannot cross as R varies), to build-up a correlation table. However, if one uses only geometrical symmetries as we have done in classifying the various states, then this usual non-crossing rule does not hold for o.e.d.ms (Gershtein & Krivchenkov 1961; Moiseiwitsch 1961). This pecularity has been explained by Alliluev & Matveenko (1966) and Coulson & Joseph (1967), who showed that there is an additional constant of motion in the two-centre Coulomb problem. When potential curves for states of the same geometrical symmetries cross (for example, the $2s\sigma_g$ and $3d\sigma_g$ states of H_2^+), their values of the quantum number corresponding to the additional constant of motion differ.

Both the inner and outer equation are of the form

$$\frac{\mathrm{d}}{\mathrm{d}x} P(x) \frac{\mathrm{d}\psi}{\mathrm{d}x} + Q(x)\,\psi(x) = 0. \tag{27}$$

The transformation

$$\psi(x) = \Phi(t(x))/\sqrt{\{P(x)\,t'(x)\}} \tag{28}$$

(Gershtein, Ponomarev & Puzynina 1965), where Φ and t are for the moment arbitrary functions and a prime on a function will denote differentiation with respect to x, results in the 'normal' form of ordinary second-order differential equation for Φ, with no first derivatives,

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}t^2} + \left(\frac{Q(x) - \frac{1}{2}P''(x)}{P(x)\,(t'(x))^2} - \frac{t'''(x)}{2(t'(x))^3} + \frac{3(t''(x))^2}{4(t'(x))^4} + \left(\frac{P'(x)}{2P(x)\,t'(x)} \right)^2 \right) \Phi(t(x)) = 0. \tag{29}$$

We remove the arbitrariness in Φ and t by specifying one or the other. The most common choice is to simply use $t(x) = x$, and then Φ satisfies

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}x^2} + \left(\frac{Q(x) - \frac{1}{2}P''(x)}{P(x)} + \left(\frac{P'(x)}{2P(x)} \right)^2 \right) \Phi(x) = 0. \tag{30}$$

† For a rigorous derivation of the von Neumann–Wigner non-crossing rule and a discussion of the shortcomings of earlier proofs, see Razi-Naqvi & Byers-Brown (1972).

In their quasi-classical J.W.K.B. treatment of the outer equation, Bates & Reid (1968) took $t(x) = \ln(x-1)$. Gershtein *et al.* (1965) carried out a quasi-classical treatment of both the inner and outer equations with

$$t(x) = \pm \int \mathrm{d}x/P(x), \tag{31}$$

which gives

$$\mathrm{d}^2\Phi/\mathrm{d}t^2 + P(x)\,Q(x)\,\Phi(t(x)) = 0. \tag{32}$$

On the other hand, if $M(t)$ satisfies an equation of the form

$$\mathrm{d}^2M/\mathrm{d}t^2 + G(t)\,M(t) = 0, \tag{33}$$

then choosing $\Phi = M$ gives an equation for $t(x)$. This is the approach followed by Komarov & Slavyanov (1967, 1968) in their work on large R asymptotic expansions.

There are several well-known properties of the bound state solutions of the Schrödinger equation for one-dimensional motion,

$$\mathrm{d}^2\psi/\mathrm{d}x^2 + (\epsilon - U(x))\,\psi(x) = 0 \tag{34}$$

(Landau & Lifshitz 1965; Condon & Morse 1929). *None of the energy levels of the discrete spectrum are degenerate.* If we label the eigenvalues in ascending order, then the '*oscillation theorem*' requires that *the n-th eigenfunction has* $n-1$ *nodes*. For the inner equation, (30) gives

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}\eta^2} + \left(-p^2 + \frac{C - R(Z_\mathrm{a} - Z_\mathrm{b})\,\eta}{1-\eta^2} + \frac{1-m^2}{1-\eta^2}\right)\Phi(\eta) = 0, \tag{35}$$

in which $-p^2$ assumes the role of the energy ϵ in (34). Holding the nodal quantum numbers and nuclear charges fixed and allowing R to vary in (35), we see that as a consequence of these two theorems the number of nodes in $Y(\eta)$ cannot change as R varies for all *finite* R. Similarly, nodes in $X(\xi)$ are conserved; the factor $\exp(\pm im\phi)$ is independent of R, so n_ϕ is trivially conserved.

Morse & Stueckelberg (1929) used conservation of nodes to correlate u.a. and s.a. states of homonuclear o.e.d.ms. Gershtein & Krivchenkov (1961) extended the results to heteronuclear o.e.d.ms. I have discovered an alternative, in some respects more fundamental, derivation of these results. To bring out the essential differences, I shall first briefly recapitulate this previous work.

Morse & Stueckelberg equated the u.a. and s.a. values for n_ξ and n_η as given by (24) and (25), getting

$$\left.\begin{aligned} n-l-1 &= N-K-m-1, \\ l-m &= \text{either} \begin{cases} 2K \\ 2K+1 \end{cases}. \end{aligned}\right\} \tag{36}$$

Solving for N and K in terms of nlm,

$$K = [\tfrac{1}{2}(l-m)], \quad N = n-l+m+K, \tag{37}$$

where $[x]$ is the integer part of x.

The heteronuclear case is more difficult because nodes are *not* necessarily conserved when R becomes *infinite*, so we cannot simply equate n_ξ and n_η in (24) and (26) to get the correct correlation rules. This loss of nodes has been noted but ignored by previous workers. Gershtein & Krivchenkov only considered the possibility that nodes could vanish if two or more coalesced to form a multiple root. If $Y(\eta)$ had a multiple root at $\eta = \gamma$ for R finite then $Y(\gamma) = \mathrm{d}Y/\mathrm{d}\eta|_{\eta=\gamma} = 0$,

and from (4) and derivatives of (4), $\mathrm{d}^k Y/\mathrm{d}\eta^k|_{\eta=\gamma} = 0$ for $k = 2, 3, 4, \ldots$. A Taylor series expansion about $\eta = \gamma$ then gives $Y(\eta) = 0$ for all η, so a multiple root is forbidden, at least for R finite. Nodes need not coalesce in order to disappear. If $Y(\eta) \to 0$ for all $\eta > 0$ as $R \to \infty$, then any nodes in $0 < \eta < 1$ for R large and finite will vanish when R is infinite.

There is a heuristic physical explanation for these disappearing nodes. Since the discrete eigenvalues of our one-dimensional differential equations are non-degenerate, the eigenfunctions must be orthogonal. Labelled according to increasing eigenvalues, the nth eigenfunction of a particular geometrical symmetry must have at least $n-1$ nodes for R finite in order to be orthogonal to the $n-1$ functions of the same symmetry with lower energies. When R is infinite, functions on centre a are automatically orthogonal to functions on centre b, and do not require nodes to be mutually orthogonal. Superfluous nodes vanish. For example, the $1s\sigma$ ground state of HeH^{2+} dissociates into H^+ plus He^+ in its ground state, and the $2p\sigma$ state dissociates into He^{2+} plus H in its ground state. For R large and finite, the $2p\sigma$ state has a node in $Y(\eta)$ near the He nucleus so that the two wavefunctions can be orthogonal; when R becomes infinite, this node vanishes. In the homonuclear case, with two-centre functions of the form (19), nodes in $Y(\eta)$ must be conserved in order to maintain orthogonality.

Gershtein & Krivchenkov (1961) considered R large and finite, so that nodes are conserved, and solved for the dominant terms near each centre in an asymptotic expansion of $Y(\eta)$. For the case where the o.e.d.m. dissociates with the electron on centre a and (21) is not satisfied by any allowable value of N_b, the wavefunction near $\eta = -1$ is essentially of the form in (18), with K_a nodes. For η near $+1$, they found

$$Y(\eta) \simeq (1-\eta)^{\frac{1}{2}m} M(-K_a + N_a(Z_a - Z_b)/Z_a, m+1, \zeta_a R(1-\eta)) \exp(\zeta_a R\eta), \tag{38}$$

where $M(\alpha, \beta, x)$ is the confluent hypergeometric function,

$$M(\alpha, \beta, x) = 1 + \frac{\alpha x}{\beta} + \frac{\alpha(\alpha+1)\, x^2}{2!\beta(\beta+1)} + \ldots \tag{39}$$

(Abramowitz & Stegun 1964). The number of nodes in $Y(\eta)$ near $\eta = +1$ depends upon the value of $-K_a + N_a(Z_a - Z_b)/Z_a$; adding this contribution to K_a gives the total which must be equal to n_η from the u.a. Nodes in $X(\xi)$ are conserved even for R infinite, so we equate n_ξ in (24) and (26) and have the desired u.a.–s.a. correlation. The centre b case is similar. When (21) holds, Gershtein & Krivchenkov expressed the wavefunction as a linear combination of Ψ^a and Ψ^b and the analysis is more complicated.

Both of these derivations required knowledge of the dominant terms in the wavefunctions at $R = 0$ and R large, and then simply counted up the nodes. In both, there is the unstated assumption that higher order corrections to the dominant term for R large would only move the positions of the nodes and not change their number. While reasonable, this assumption is difficult to prove; its lack of proof leaves these results incomplete. I have discovered an alternative derivation of the correlations which avoids this difficulty; we do not require detailed knowledge about the form of the wavefunction, but only that it is separable as in (3). I shall continue to use the u.a. and s.a. quantum numbers in order to compare my results with the previous work; this assumes only that we know (24) and (26) relating them to the nodal quantum numbers.

U.A.–S.A. CORRELATION FROM THE O.E.D.M. NON-CROSSING RULE

We can easily prove the following o.e.d.m. non-crossing rule, which is a consequence of the separability of the wavefunction in elliptic coordinates. Let Z_a and Z_b be fixed and, for finite R, let states 1 and 2 be characterized by their nodal quantum numbers n_ξ, n_η, n_ϕ and n'_ξ, n'_η and n'_ϕ. *In order for the potential curves of these to states to cross, at least two of the three nodal quantum numbers must be different.*

For instance, consider $n_\xi = n'_\xi$, $n_\phi = n'_\phi$, but $n_\eta \neq n'_\eta$, and assume that the potential curves cross at $R = R_0$. The energies are equal at R_0, so the value of p is the same for both states at the point of crossing. Since $X(\xi)$ has the same number of nodes for both states, we must have exactly the same function X for both at R_0 because there are no degenerate eigenvalues of the outer equation having the same geometrical symmetry. The separation constant C must be the same for both states at R_0, and hence both have the same potential in the inner equation. But $n_\eta \neq n'_\eta$ then contradicts the non-degeneracy of the eigenvalues of (35), so such a crossing is forbidden.

On the other hand, if both $n_\xi \neq n'_\xi$ and $n_\eta \neq n'_\eta$, we have two distinct values C and C' for the separation constants. With different potentials in (35) for the two states, the theorem about non-degeneracy of eigenvalues does not apply, and crossing can occur.

A simple example will best illustrate how we can now use this o.e.d.m. non-crossing rule to build-up correlations between u.a. and s.a. states. Consider the σ states of HeH^{2+} with no nodes in $X(\xi)$, $n_\xi = n_\phi = 0$, $n_\eta = 0, 1, 2, \ldots$, i.e. $1s\sigma$, $2p\sigma$, $3d\sigma$, ... Starting with $n_\eta = 0$, we require that each state dissociates into the lowest available s.a. state consistent with conservation of n_ξ and n_ϕ and also with the o.e.d.m. non-crossing rule. The ground state thus dissociates into

$$H^+ + He^+ (100)\ (N = 1, K = m = 0).$$

The $2p\sigma$ state presents a momentary dilemma, because both $H(100) + He^{2+}$ and $H^+ + He^+(210)$ have $W(\infty) = -0.5$ a.u. However, by using (23), for R large and finite the first state goes as $W(R) = -0.5 - 2/R + \ldots$, the second as $-0.5 - 1/R + \ldots$. Since these curves cannot cross (their equality at $R = \infty$ is not a crossing), the $2p\sigma$ state must dissociate into the s.a. state with lower energy at finite R, $H(100) + He^{2+}$. The next state, $3d\sigma$, then becomes $H^+ + He^+(210)$. One sees that in those cases where $Z_a/N_a = Z_b/N_b$ with $Z_a > Z_b$, the state with the electron on centre b is always lower in energy for finite R, and is filled first when we build-up the correlation table.

By formalizing this 'counting' of the states, we easily find analytical expressions relating the u.a. and s.a. quantum numbers. Assume that $Z_a > Z_b$, and let the u.a. quantum numbers nlm be given, so that n_ξ, n_η, and n_ϕ are given by (24). Restricting n_ξ and n_ϕ to these particular values, we simplify notation by labelling the s.a. states on a and b only by their parabolic quantum numbers, K_a and K_b. The s.a. total quantum numbers are

$$N_a = n_\xi + K_a + m + 1, \quad N_b = n_\xi + K_b + m + 1, \tag{40}$$

and the s.a. energies are

$$W^a_{K_a}(\infty) = -Z_a^2/2N_a^2, \quad W^b_{K_b}(\infty) = -Z_b^2/2N_b^2. \tag{41}$$

There are $l - m - 1$ states with lower energies and the same number of nodes n_ξ and n_ϕ, and we now consider $n_\eta = 0, 1, \ldots, l - m$. The first state, $n_\eta = 0$, dissociates onto centre a with $K_a = 0$, and states continue to go onto centre a until we reach the first value of K_a for which

$$Z_b/(n_\xi + m + 1) \geqslant Z_a/(n_\xi + K_a + m + 1), \tag{42}$$

at which point we get a state with $K_b = 0$ on centre b. In general, we must have both

$$Z_b/(n_\xi + K_b + m + 1) \geqslant Z_a/(n_\xi + K_a + m + 1) \tag{43}$$

and $$Z_b/(n_\xi + K_b + m + 1) < Z_a/(n_\xi + K_a + m) \tag{44}$$

in order that the $(K_a + K_b + 1)th$ state should be on centre b. Since we are interested in the $(l - m + 1)th$ state, we set

$$K_a + K_b = l - m. \tag{45}$$

Solving (43) for K_b, we find

$$K_b = [(Z_b(n+1) - Z_a(n - l + m - 1))/(Z_a + Z_b)] - 1, \tag{46}$$

where again $[x]$ is the integer part of x.

If (46) gives $K_b < 0$, this simply means that we do not get a single state on centre b in the s.a. limit from the first $l - m + 1$ u.a. states. Suppose then that K_b from (46) is $\geqslant 0$. We can tell whether the appropriate s.a. centre is a or b by testing the $(l - m)$th state, as in (44). The electron will be on centre a if

$$(Z_b n - Z_a(n - l + m - 1))/(Z_a + Z_b) \geqslant 1 + K_b, \tag{47}$$

and then $$K_a = l - m - K_b. \tag{48}$$

In either case, the total quantum number is given by (40).

This establishes the desired one-to-one correlation between u.a. and s.a. states of heteronuclear o.e.d.ms. Although we worked under the assumption that $Z_a > Z_b$, the same type of procedure works when $Z_a = Z_b$. Simply setting $Z_a = Z_b$ in (46) gives $K = [\frac{1}{2}(l - m)]$, in agreement with (37). It is also useful to have formulae expressing the u.a. quantum numbers in terms of Z_a, Z_b and the s.a. quantum numbers. Inverting these results, we find (still assuming that $Z_a > Z_b$)

$$\text{s.a. on centre } b \begin{cases} n = \begin{cases} K_b + N_b Z_a/Z_b & \text{if} \quad N_b Z_a/Z_b = \text{integer}, \\ K_b + 1 + [N_b Z_a/Z_b] & \text{otherwise}, \end{cases} \\ l = n + m + K_b - N_b, \end{cases} \tag{49}$$

$$\text{s.a. on centre } a \begin{cases} \begin{cases} n = N_a \\ l = K_a + m \end{cases} & \text{if} \quad K_a < N_a(Z_a - Z_b)/Z_a, \\ \begin{cases} l = K_a + m + 1 + [K_a - N_a(Z_a - Z_b)/Z_a] \\ n = l + N_a - K_a - m \end{cases} & \text{otherwise.} \end{cases} \tag{50}$$

These latter results are equivalent to the correlation rules found by Gershtein & Krivchenkov.†

Several authors have previously noted that the heteronuclear o.e.d.m. results of Gershtein & Krivchenkov are consistent with the non-degeneracy of eigenvalues and oscillation theorem for the one-dimensional equations. Komarov & Slavyanov (1968) have in fact stated the o.e.d.m. non-crossing rule, but seem to treat it as a consequence of the Gershtein & Krivchenkov results rather than as the fundamental assertion which it rightfully is.

Asymptotic expansion of $W(R)$

Expansions of $W(R)$ as a power series in R for R small and $1/R$ for R large can be quite useful. In their ranges of validity, they dispense with the need for huge tables of numerically obtained energies. The large R expansion will also enable us to give a detailed treatment and interpretation of quasi-crossings of potential curves.

† There is a typographical error in equation (41) of the English translation of their paper; the $\geqslant$ and $<$ should be interchanged.

Using united atom short-range perturbation theory (Byers-Brown 1968; Byers-Brown & Power 1970), Byers-Brown, Chang, and Power have obtained analytical expressions in terms of the nuclear charges and u.a. numbers for the coefficients through W_4 in the expansion

$$W(R) = W_0 + R^2W_2 + R^3W_3 + R^4W_4 + \ldots. \tag{51}$$

The details of this work will be published elsewhere. Byers-Brown & Steiner (1966) showed that the next term in (51) is of order $R^5 \ln R$.

Several different approaches have been used to obtain the large R expansion of $W(R)$ in powers of $1/R$. Dalgarno & Lewis (1956) have shown that such an expansion must be asymptotic. Dalgarno and co-workers (1955–7) and Robinson (1958) used perturbation theory, with the term Z_b/r_b in (1) taken as the perturbation, and expanded the perturbation energies in powers of $1/R$. The complexity of the analysis has restricted these calculations to the four lowest states, with $N_aK_am = 100$, 201, 200 and 210. Coulson & Gillam (1947) carried out a perturbation calculation in which they found expansions of $W(R)$ through $O(1/R^5)$ for arbitrary states of H_2^+. However, they incorrectly used atomic wavefunctions in parabolic coordinates for their zero-order wavefunctions, instead of in the proper elliptic coordinates (Coulson & Robinson 1958), and their term of $O(1/R^5)$ is in error (Robinson 1958).

An alternative approach is to somehow obtain asymptotic expansions of C/p in powers of $1/p$ directly from the inner and outer equations. Denoting these two expansions as $\tilde{C}_\xi$ and $\tilde{C}_\eta$, equating $\tilde{C}_\xi$ and $\tilde{C}_\eta$ gives an equation involving only p, R, Z_a, Z_b and the nodal quantum numbers, which we can solve for p/R as a power series in $1/R$, and square to get $W(R)$. The tremendous advantage of this approach is that we can carry through the analysis using arbitrary nodal quantum numbers, and thus obtain a general formula, as opposed to the treatment of each state individually in the perturbation calculations.

Komarov & Slavyanov (1967, 1968) used the modified comparison method (Slavyanov 1967) to obtain asymptotic expansions of $X(\xi)$ and $Y(\eta)$, and in turn from these the expansions $\tilde{C}_\xi$ and $\tilde{C}_\eta$. They determined the expansion of $W(R)$ through $O(1/R^4)$. Their method could be extended to evaluate higher order terms, but doing so would require considerably more effort than does the approach which I shall now present.

Assuming that R is large, we take the square root of (23) and find the approximation for a s.a. state on centre a,

$$p = RZ_a/2N_a + N_aZ_b/2Z_a + \ldots. \tag{52}$$

In the following work, we shall assume that

$$R \gg 2N_a/Z_a, \tag{53}$$

so that p will be large. We already know the limiting form Ψ^a for a s.a. state, and will now expand $X(\xi)$ and $Y(\eta)$ in forms that can easily reduce to this limit as $R \to \infty$. We express $X(\xi)$ as

$$X(\xi) = (\xi^2 - 1)^{\frac{1}{2}m} \exp(-p(\xi - 1))\, L(2p(\xi - 1)). \tag{54}$$

Making the change of variable

$$x = 2p(\xi - 1) \quad (0 \leqslant x \leqslant \infty), \tag{55}$$

we find that $L(x)$ satisfies the differential equation

$$(\mathscr{L}(x, p, m, S) - C)\, L(x) = 0, \tag{56}$$

where

$$\mathscr{L}(x, p, m, S) = x(x + 4p)\,(\mathrm{d}^2/\mathrm{d}x^2) + (-x^2 + 2x(m + 1 - 2p) + 4p(m + 1))\,(\mathrm{d}/\mathrm{d}x) + m(m + 1) - 2p(m + 1 - S)\,(1 + x/2p) \tag{57}$$

and $$S = R(Z_a + Z_b)/2p. \tag{58}$$

We will use two forms of solution for the inner equation, one appropriate when the electron is near centre $a(\eta = -1)$, the other for centre b. The centre a expansion is

$$Y_-(\eta) = (1-\eta^2)^{\frac{1}{2}m} \exp(-p(1+\eta))\, \Lambda_-(2p(1+\eta)). \tag{59}$$

Introducing the new variable

$$y = 2p(1+\eta) \quad (0 \leqslant y \leqslant 4p), \tag{60}$$

we obtain $$(\mathscr{L}(y, -p, m, D) - C)\, \Lambda_-(y) = 0, \tag{61}$$

where $$D = R(Z_a - Z_b)/2p. \tag{62}$$

The centre b expansion is

$$Y_+(\eta) = (1-\eta^2)^{\frac{1}{2}m} \exp(-p(1-\eta))\, \Lambda_+(2p(1-\eta)), \tag{63}$$

and defining $$z = 2p(1-\eta) \quad (0 \leqslant z \leqslant 4p) \tag{64}$$

gives $$(\mathscr{L}(z, -p, m, -D) - C)\, \Lambda_+(z) = 0. \tag{65}$$

Actually, either form of solution, (59) or (63), could be used for the entire range of η. We will solve for $\Lambda_\pm$ by series expansions, and, with appropriate choice of expansion functions, just a single term in the expansion of Λ_- will be a good description of Λ_- near $\eta = -1$, and similarly for Λ_+ near $\eta = +1$. However, to evaluate Λ_- accurately near $\eta = +1$ would require a large number of terms, hence it is useful to have the two different expansions. Similar reasoning led Bates & Carson (1956) to use two expansions for $Y(\eta)$ in their work on HeH^{2+} (they noted potential differencing errors).

Equation (56) has a regular singularity at $x = 0$ and an essential singularity at $x = \infty$. Equations (61) and (65) have regular singularities at y or z equal to 0 and $4p$; when R becomes infinite, the singularity at $4p$ becomes an essential singularity.† Because of the infinite range of x, we shall find that $L(x)$ must be a polynomial in x. On the other hand, $\Lambda_\pm$ can have exponentially increasing terms in y or z for R finite. In spite of these important differences between the inner and outer equations, we will be able to exploit the symmetry between these equations, to obtain $\tilde{C}_\eta$ from $\tilde{C}_\xi$ (or vice versa).

Dividing (56) by $4p$, we get

$$\left(x\frac{d^2}{dx^2} + (m+1-x)\frac{d}{dx} + \tfrac{1}{2}(S-m-1-C/2p)\right) L(x)$$
$$= -\frac{1}{4p}\left(x^2\frac{d^2}{dx^2} + (2(m+1)\,x - x^2)\frac{d}{dx} + m(m+1) - (m+1-S)\,x\right) L(x). \tag{66}$$

For p very large, we can get a good first approximation for $L(x)$ by ignoring the right-hand side of (66). The confluent hypergeometric function satisfies

$$\left(x\frac{d^2}{dx^2} + (\beta - x)\frac{d}{dx} - \alpha\right) M(\alpha, \beta, x) = 0, \tag{67}$$

so $$L(x) \simeq M(\tfrac{1}{2}(m+1-S+C/2p), m+1, x). \tag{68}$$

For $x \gg 0$, we can use the asymptotic expansion

$$M(\alpha, \beta, x) = \frac{\Gamma(\beta)\,(-x)^{-\alpha}}{\Gamma(\beta-\alpha)}\left\{\sum_{j=0}^{J} \frac{(\alpha)_j\,(1+\alpha-\beta)_j}{j!\,(-x)^j} + O\left(\frac{1}{x^{J+1}}\right)\right\}$$
$$+ \frac{\Gamma(\beta)\,x^{\alpha-\beta}\,e^x}{\Gamma(\alpha)}\left\{\sum_{j=0}^{J'} \frac{(\beta-\alpha)_j\,(1-\alpha)_j}{j!\,x^j} + O\left(\frac{1}{x^{J'+1}}\right)\right\}, \tag{69}$$

† The possible loss of nodes in $Y(\eta)$ when R becomes infinite may be connected with this change in the character of the singularity in the differential equations for $\Lambda_\pm$.

where $\Gamma(\beta)$ is the usual gamma function, J and J' signify that we truncate these divergent summations after a few terms, and $(\alpha)_j$ is Pochhammer's symbol,

$$(\alpha)_0 = 1, \quad (\alpha)_j = \alpha(\alpha+1)\ldots(\alpha+j-1) = \Gamma(\alpha+j)/\Gamma(\alpha). \tag{70}$$

Since

$$\frac{(n_\xi+m)!}{n_\xi!\,m!} M(-n_\xi, m+1, x) = L^m_{n_\xi}(x) \simeq L^m_{n_\xi}((RZ_a/N_a+\ldots)(\xi-1)), \tag{71}$$

the form needed in (18), we see that

$$\tfrac{1}{2}(S-m-1-\tilde{C}_\xi/2p) = n_\xi+\delta n_\xi, \tag{72}$$

where δn_ξ goes to zero as $R \to \infty$. For δn small, the identity

$$\Gamma(\alpha)\,\Gamma(1-\alpha) = \pi/\sin(\pi\alpha) \tag{73}$$

gives

$$1/\Gamma(-n-\delta n) \simeq (-1)^{n+1} n!\,\delta n. \tag{74}$$

Keeping only the two largest groups from (69),

$$M(-n-\delta n, m+1, x) \simeq \frac{n!\,m!}{(n+m)!} L^m_n(x) + \frac{(-1)^{n+1} m!\,e^x\,\delta n}{(m+n)!\,x^{n+m+1}} \sum_{j=0}^{J'} \frac{(n+j)!\,(n+m+j)!}{j!\,x^j}. \tag{75}$$

In deriving (75), we have ignored terms of $O(\delta n)$ from the first factor in (69); this is justified because these terms do not have the large $\exp(x)$ multiplying them, and are truly negligible compared to the second group in (75).† We see that with $L(x)$ we must have $\delta n_\xi = 0$ even for R finite, otherwise the second term in (75) would give a $X(\xi)$ which diverged as $\exp(p\xi)$ as $\xi \to \infty$. Thus, as our initial approximation,

$$\tilde{C}_\xi \simeq -2p(2n_\xi+m+1)+2pS. \tag{76}$$

In a completely analogous fashion, we find the initial approximations

$$\Lambda_-(y) \simeq M(\tfrac{1}{2}(m+1-D-C/2p),\ m+1, y) \tag{77}$$

and

$$\Lambda_+(z) \simeq M(\tfrac{1}{2}(m+1+D-C/2p),\ m+1, z). \tag{78}$$

For a centre a s.a. state, requiring that Λ_- reduce to $L^m_{K_a}$ as $R \to \infty$ gives

$$C_\eta \simeq 2p(2(K_a+\delta n_\eta)+m+1)-2pD, \tag{79}$$

where $\delta n_\eta \to 0$ as $R \to \infty$. However, for finite R, in contrast to the outer equation, we need not and cannot take $\delta n_\eta = 0$. A non-zero δn_η is required so that $\Lambda_\pm$ can satisfy their boundary conditions. We can take p so large that most of the nodes in $Y(\eta)$ are concentrated near $\eta = \pm 1$, and then we match-up Λ_+ and Λ_- and their derivatives at some intermediate value of η; using $\eta = 0$ will usually be the most convenient. For instance, for $Y(\eta)$ odd in a homonuclear o.e.d.m., we require that $\Lambda_\pm(2p) = 0$. Using (75) for $\Lambda_\pm$, if we take $\delta n_\eta \sim \exp(-2p)$, the two terms will be of comparable magnitude and can cancel to give zero. For a centre a s.a. state of a heteronuclear o.e.d.m., we must have $\delta n_\eta \sim \exp(-4p)$, otherwise $Y(\eta)$ will be too large near $\eta = +1$. In all cases, δn_η must be exponentially small in p, and cannot go to zero merely as some power of $1/p$. Since $\exp(-p)$ does not contribute to an asymptotic expansion in powers of $1/p$, we will be able to ignore δn_η when we find $\tilde{C}_\eta$.

† Damburg & Propin (1968) give this expansion including all the terms of order δn. The gamma functions in the first summation of their equation (22) should be multiplied rather than subtracted.

By analogy with the results for Λ_-, we *define* $\bar{K}_b$ for Λ_+ by

$$\bar{K}_b + \delta n_\eta = \tfrac{1}{2}(C/2p - m - 1 - D). \tag{80}$$

Note that

$$K_a - \bar{K}_b = D. \tag{81}$$

K_a is an integer, but $\bar{K}_b$ will usually be non-integral. Using (52), we have

$$D \simeq N_a(Z_a - Z_b)/Z_a, \tag{82}$$

and

$$\Lambda_+(z) \simeq M(-K_a + N_a(Z_a - Z_b)/Z_a,\ m+1,\ RZ_a(1-\eta)/N_a). \tag{83}$$

These results essentially reproduce those found by Gershtein & Krivchenkov in their work correlating u.a. and s.a. states; thus far our treatment closely parallels their analysis.

We now return to the outer equation. To find the higher order terms in $\tilde{C}_\xi$, we make the expansion

$$L(x) = \sum_{j=0}^{\infty} g_j L_j^m(x) \tag{84}$$

(Hylleraas 1931). If we take the operator on the left of (66) to be the zero-order Hamiltonian, and that on the right as the perturbation, then $\{L_j^m(x)\}$ is the complete set of zero-order eigenfunctions and (84) is equivalent to the expansion of the total wavefunction in the set of zero-order functions. Rather than use the framework of perturbation theory to find the expansion coefficients, we simply substitute (84) into (56) and find that the g_j must satisfy the three-term recurrence relation

$$\alpha_i g_{i-1} + \beta_i g_i + \gamma_i g_{i+1} = 0, \tag{85}$$

where

$$\left.\begin{aligned} \alpha_i &= i(i+m) - iS, \\ \beta_i &= -C + 2p(S - 2i - m - 1) + S(2i+m+1) - 2i^2 - 2im - 2i - m - 1, \\ \gamma_i &= (i+1)(i+m+1) - (i+m+1)S, \end{aligned}\right\} \tag{86}$$

and with boundary condition that $g_{-1} = 0$. Baber & Hassé (1935) have proved the convergence of this expansion.

We can use either Λ_- or Λ_+ to find the asymptotic expansion $\tilde{C}_n$. The expansion

$$\Lambda_-(y) = \sum_{j=0}^{\infty} h_j M(-(j+\delta n_\eta), m+1, y) \tag{87}$$

leads to a three-term recurrence relation analogous to (85), with

$$\left.\begin{aligned} \alpha_i &= (i+\delta n_\eta + m)(i+\delta n_\eta + m - D), \\ \beta_i &= -C + 2p(2(i+\delta n_\eta) + m + 1 - D) - 2(i+\delta n_\eta)(i+\delta n_\eta + m + 1 - D) \\ &\qquad - (m+1)(1-D), \\ \gamma_i &= (i+\delta n_\eta + 1)(i+\delta n_\eta + 1 - D). \end{aligned}\right\} \tag{88}$$

A similar expansion for Λ_+ results in the replacement of D by $-D$ in (88). Having more than one term in the expansion does not invalidate our previous conclusions about the magnitude of δn_η; also, we still require only a single δn_η to satisfy the boundary conditions.

We begin by converting the three-term recurrence relation into an equivalent continued fraction (Baber & Hassé 1935; Chakravarty 1939; Gautschi 1967). Replacing i by $i+1$ in (85) and solving for g_{i+1}/g_i,

$$g_{i+1}/g_i = -\alpha_{i+1}/(\beta_{i+1} + \gamma_{i+1} g_{i+2}/g_{i+1}). \tag{89}$$

We have similar expressions for g_{i+2}/g_{i+1}, g_{i+3}/g_{i+2}, ..., and when these are substituted in turn into (89), we obtain the infinite continued fraction

$$\gamma_i g_{i+1}/g_i = -\frac{\gamma_i\alpha_{i+1}}{\beta_{i+1}-}\,\frac{\gamma_{i+1}\alpha_{i+2}}{\beta_{i+2}-}\,\frac{\gamma_{i+2}\alpha_{i+3}}{\beta_{i+3}-}\cdots. \tag{90}$$

Similarly, we get the finite continued fraction

$$\alpha_i g_{i-1}/g_i = -\frac{\gamma_{i-1}\alpha_i}{\beta_{i-1}-}\,\frac{\gamma_{i-2}\alpha_{i-1}}{\beta_{i-2}-}\cdots\frac{\gamma_0\alpha_1}{\beta_0}. \tag{91}$$

Dividing (85) by g_i and using (90) and (91),

$$\beta_i - \frac{\gamma_{i-1}\alpha_i}{\beta_{i-1}-}\,\frac{\gamma_{i-2}\alpha_{i-1}}{\beta_{i-2}-}\cdots\frac{\gamma_0\alpha_1}{\beta_0} - \frac{\gamma_i\alpha_{i+1}}{\beta_{i+1}-}\,\frac{\gamma_{i+1}\alpha_{i+2}}{\beta_{i+2}-}\cdots = 0. \tag{92}$$

In the limit $R\to\infty$, only the coefficient g_{n_ξ} remains finite, so to avoid singularities in the ratios $g_{i\pm1}/g_i$ in (92), we must use $i = n_\xi$. We can formally solve (92) for the separation constant; let us denote the solution as $C_\xi(p, S, n_\xi, m)$. When we use (92) for Λ_-, we must take $i = K_a$, and we denote the solution as $C_\eta(p, D, K_a+\delta n_\eta, m)$. Making the replacements $p\to -p$, $S\to D$, and $i\to i+\delta n_\eta$ in (86), we find that $\gamma_i\alpha_{i+1}$ and β_i from (86) are identical to those from (88). We thus must have

$$C_\eta(p, D, K_a+\delta n_\eta, m) = C_\xi(-p, D, K_a+\delta n_\eta, m), \tag{93}$$

so we can focus our attention on C_ξ and then get C_η by symmetry.

Consider an infinite continued fraction of the form

$$f = \frac{a_1}{b_1+}\,\frac{a_2}{b_2+}\,\frac{a_3}{b_3+}\cdots. \tag{94}$$

Defining the truncated continued fraction

$$f_N = \frac{a_1}{b_1+}\,\frac{a_2}{b_2+}\cdots\frac{a_N}{b_N}, \tag{95}$$

the value of the infinite continued fraction is defined as

$$f = \lim_{N\to\infty} f_N, \tag{96}$$

if this limit exists. We define the jth numerators A_j and denominators B_j by the recurrence relations

$$\left.\begin{aligned} A_j &= b_j A_{j-1} + a_j A_{j-2},\\ B_j &= b_j B_{j-1} + a_j B_{j-2},\end{aligned}\right\} \tag{97}$$

for $j = 1, 2, \ldots$, with initial values

$$A_{-1} = 1, \quad A_0 = 0, \quad B_{-1} = 0, \quad B_0 = 1. \tag{98}$$

One can easily prove by induction (Wall 1948) that

$$f_N = A_N/B_N. \tag{99}$$

For our present purpose, it is more convenient to rewrite this as

$$f_N = \frac{A_1}{B_1} + \left(\frac{A_2}{B_2} - \frac{A_1}{B_1}\right) + \ldots + \left(\frac{A_N}{B_N} - \frac{A_{N-1}}{B_{N-1}}\right), \tag{100}$$

and use the result (Blanch 1964) that

$$\frac{A_j}{B_j}-\frac{A_{j-1}}{B_{j-1}}=\frac{(-1)^j a_1 a_2 a_3 \dots a_j}{B_j B_{j-1}} \tag{101}$$

to get

$$f=\frac{a_1}{B_0 B_1}-\frac{a_1 a_2}{B_1 B_2}+\frac{a_1 a_2 a_3}{B_2 B_3}-\frac{a_1 a_2 a_3 a_4}{B_3 B_4}+\dots. \tag{102}$$

As we shall see, each successive term $(-1)^j a_1 a_2 \dots a_j / B_j B_{j-1}$ in (102) is of $O(1/p^2)$ smaller than the previous term, as long as $j \ll p$, and this furnishes us with a well-defined scheme for evaluating C_ξ by the method of successive approximations. Taking $i = n_\xi$ in (92), it turns out that the results can be expressed most compactly in terms of the parameter

$$\nu = 2i+m+1 = 2n_\xi+m+1, \tag{103}$$

in addition to p, S, and m. It is expedient to introduce at this time a notation which is motivated by a discussion given in appendix 2 relating the successive approximations to perturbation theory. We define the matrix elements of V and E^0 by

$$V_{i+k+1,\,i+k} = \alpha_{i+k+1} = \tfrac{1}{4}(\nu^2+(2+4k)\,\nu-m^2+(1+2k)^2)-\tfrac{1}{2}S(\nu+1+2k-m), \tag{104}$$

$$V_{i+k,\,i+k+1} = \gamma_{i+k} = \tfrac{1}{4}(\nu^2+(2+4k)\,\nu-m^2+(1+2k)^2)-\tfrac{1}{2}S(\nu+1+2k+m), \tag{105}$$

$$V_{i+k,\,i+k} = S(\nu+2k)-\tfrac{1}{2}(\nu^2+1-m^2)-2k(\nu+k), \tag{106}$$

$$V'_{i+k,\,i+k'} = V_{i+k,\,i+k'}-\delta_{k,k'}V_{i,\,i}, \tag{107}$$

$$E^0_{i+k} = 2(S-\nu-2k), \tag{108}$$

where $k = 0, \pm 1, \pm 2, \dots$. Note that

$$\beta_{i+k} = -C+pE^0_{i+k}+V_{i+k,\,i+k}. \tag{109}$$

Comparing the general continued fraction (94) with the specific continued fractions (90) and (91), we use

$$\text{(for 90)} \quad b_k = \beta_{i+k}, \quad a_k = -V_{i+k-1,\,i+k}V_{i+k,\,i+k-1}, \tag{110}$$

$$\text{(for 91)} \quad b_k = \beta_{i-k}, \quad a_k = -V_{i+1-k,\,i-k}V_{i-k,\,i+1-k}, \tag{111}$$

with $k = 1, 2, 3, \dots$.

The ratios $g_{i\pm1}/g_i$ both go to zero as $R \to \infty$, so as a reasonably good first approximation, we can ignore the two continued fractions in (92) and simply use $\beta_i = 0$ to get

$$C^{(0)}_\xi = pE^0_i+V_{ii}. \tag{112}$$

For the second approximation, we keep the lead term, a_1/b_1, of (102) for the two continued fractions in (92), and find

$$C^{(1)}_\xi = C^{(0)}_\xi-\frac{V_{i,i-1}V_{i-1,i}}{\beta_{i-1}}-\frac{V_{i,i+1}V_{i+1,i}}{\beta_{i+1}}. \tag{113}$$

We use $C^{(0)}$ from (112) to get

$$\beta_{i+k} \simeq -4pk+V'_{i+k,\,i+k} \tag{114}$$

and use this for $\beta_{i\pm1}$ when evaluating (113).

The matrix elements V are of $O(p^0)$; from (114), β_{i+k} is of $O(p^1)$. It follows from the recurrence relation (97) defining B_j that B_j is of $O(p^j)$. Thus, in (102), $B_0 B_1$ is of $O(p^1)$, $B_1 B_2$ is of $O(p^3)$, etc.,

and each successive term is of $O(1/p^2)$ smaller than the previous term. We now *assume* that we can expand C_ξ as a power series in $1/p$. From the above discussion, the higher order terms which we have neglected in forming (113) will give a contribution of $O(1/p^3)$, so we expand (113) to get

$$\tilde{C}_\xi^{(1)} = pE_i^0 + V_{ii} + \frac{1}{4p}(V_{i,i+1}V_{i+1,i} - V_{i,i-1}V_{i-1,i}) + \frac{1}{16p^2}(V_{i,i+1}V'_{i+1,i+1}V_{i+1,i} + V_{i,i-1}V'_{i-1,i-1}V_{i-1,i}). \tag{115}$$

For the next approximation, we include the second term in (102) in the two continued fractions in (92), getting

$$C_\xi^{(2)} = C_\xi^{(1)} - \frac{V_{i,i-1}V_{i-1,i-2}V_{i-2,i-1}V_{i-1,i}}{\beta_{i-1}(\beta_{i-1}\beta_{i-2} - V_{i-1,i-2}V_{i-2,i-1})} - \frac{V_{i,i+1}V_{i+1,i+2}V_{i+2,i+1}V_{i+1,i}}{\beta_{i+1}(\beta_{i+1}\beta_{i+2} - V_{i+1,i+2}V_{i+2,i+1})}, \tag{116}$$

where we now use $C_\xi^{(1)}$ to evaluate β_{i+k} in this expression. Expanding gives

$$\begin{aligned}
\tilde{C}_\xi^{(2)} = \tilde{C}_\xi^{(1)} &+ \frac{1}{128p^3}\{V_{i,i+1}V_{i+1,i}(V_{i+1,i+2}V_{i+2,i+1} + 2((V'_{i+1,i+1})^2 - V_{i,i+1}V_{i+1,i})) \\
&- V_{i,i-1}V_{i-1,i}(V_{i-1,i-2}V_{i-2,i-1} + 2((V'_{i-1,i-1})^2 - V_{i,i-1}V_{i-1,i}))\} \\
&+ \frac{1}{1024p^4}\{V_{i,i+1}V_{i+1,i+2}V'_{i+2\ i+2}V_{i+2,i+1}V_{i+1,i} + V_{i,i-1}V_{i-1,i-2}V'_{i-2,i-2}V_{i-2,i-1}V_{i-1,i} \\
&+ 4V_{i,i+1}V'_{i+1,i+1}V_{i+1,i}(V_{i+1,i+2i+2}V_{i+1} - 3V_{i,i+1}V_{i+1,i} + V_{i,i-1}V_{i-1,i} + (V'_{i+1,i+1})^2) \\
&+ 4V_{i,i-1}V'_{i-1,i-1}V_{i-1,i}(V_{i-1,i-2}V_{i-2,i-1} - 3V_{i,i-1}V_{i-1,i} + V_{i,i+1}V_{i+1,i} + (V'_{i-1,i-1})^2)\}.
\end{aligned} \tag{117}$$

We can extend these approximations to however high an order we require simply by including more terms from expansion (102) for the continued fractions.

In the derivation of these expansions, we assumed that we could expand $1/\beta_{i+k}$ as

$$\frac{1}{\beta_{i+k}} = -\frac{1}{4pk}\left(1 + \frac{V'_{i+k,i+k}}{4pk} + O\left(\frac{1}{p^2}\right)\right). \tag{118}$$

Given any value of p, this is valid only for $|k| \ll p$, because $V'_{i+k,i+k}$ is proportional to k^2. As we go to higher and higher orders, we must eventually reach $|k| > p$, so approximation (118) must break down. When this occurs, our expansion in $1/p$ will actually decrease in accuracy with additional terms. The expansion of C_ξ in powers of $1/p$, which we have denoted as $\tilde{C}_\xi$, is thus seen to be an asymptotic expansion. The approximations $C_\xi^{(0)}, C_\xi^{(1)}, C_\xi^{(2)}, \ldots$ form a well-defined convergent sequence of approximations to C_ξ, valid even for $p \to 0$, whereas the $1/p$ sequence $\tilde{C}_\xi^{(1)}, \tilde{C}_\xi^{(2)}, \ldots$ is asymptotic for p large and singular as $p \to 0$.

To evaluate $\tilde{C}_\xi^{(1)}, \tilde{C}_\xi^{(2)}, \ldots$, we merely have to multiply together various combinations of matrix elements of V. Each matrix element is a polynomial in the three variables S, ν, and m. Evaluation of the first few orders can be done by hand calculation, but the number of terms grows so rapidly that we soon have to turn to the computer. These simple polynomial multiplications were very easily programmed for computer evaluation, and in this way I have been able to extend the evaluation of $\tilde{C}_\xi$ through $O(1/p^5)$,

$$\begin{aligned}
\tilde{C}_\xi(p, S, n_\xi, m) = {} & 2p\{S - \nu\} + \{\nu S - \tfrac{1}{2}(\nu^2 + 1 - m^2)\} + \frac{1}{8p}\{\nu(\nu^2 + 1 - m^2) - (3\nu^2 + 1 - m^2)\,S + 2\nu S^2\} \\
&+ \frac{1}{64p^2}\{-5\nu^4 - 10\nu^2 + 6\nu^2m^2 - (1 - m^2)^2 + (20\nu^2 + 20 - 12m^2)\,\nu S \\
&- (24\nu^2 + 8(1 - m^2))\,S^2 + 8\nu S^3\} \\
&+ \frac{1}{512p^3}\{\nu(33\nu^4 + 114\nu^2 - 46\nu^2m^2 + 37 + 13m^4 - 50m^2)
\end{aligned}$$

$$
\begin{aligned}
&-(165\nu^4+342\nu^2-138\nu^2m^2+37+13m^4-50m^2)\,S\\
&+(284\nu^2+292-156m^2)\,\nu S^2-(192\nu^2+64(1-m^2))\,S^3+40\nu S^4\}\\
&+\frac{1}{1024p^4}\{-63\nu^6-340\nu^4-239\nu^2-14+100\nu^4m^2-39\nu^2m^4+230\nu^2m^2\\
&+2m^6-18m^4+30m^2+(378\nu^4+1360\nu^2+478-400\nu^2m^2-460m^2+78m^4)\,\nu S\\
&-(845\nu^4+1810\nu^2+209-630\nu^2m^2-250m^2+41m^4)\,S^2+(860\nu^2+900-460m^2)\nu S^3\\
&-(384\nu^2+128(1-m^2))\,S^4+56\nu S^5\}\\
&+\frac{1}{8192p^5}\{\nu(527\nu^6+4139\nu^4+5221\nu^2+1009-939\nu^4m^2+465\nu^2m^4\\
&-3750\nu^2m^2-53m^6+635m^4-1591m^2)\\
&-(3689\nu^6+20\,695\nu^4+15\,663\nu^2+1009-4695\nu^4m^2+1395\nu^2m^4\\
&-11\,250\nu^2m^2-53m^6+635m^4-1591m^2)\,S\\
&+(10\,128\nu^4+37\,640\nu^2+14\,072-9520\nu^2m^2-11\,640m^2+1440m^4)\,\nu S^2\\
&-(13\,750\nu^4+30\,140\nu^2+3630-9780\nu^2m^2-4140m^2+510m^4)\,S^3\\
&+(9520\nu^2+10\,080-5040m^2)\,\nu S^4-(3072\nu^2+1024(1-m^2))\,S^5\\
&+336\nu S^6\}+\ldots.
\end{aligned}
\tag{119}
$$

We now obtain $\tilde{C}_\eta$ by symmetry, using (93). Since δn_η is exponentially small in p, we see that we can set it equal to zero as far as the inner equation analogue of (119) is concerned. C must be the same in both the inner and outer equations, so the next step is to equate $\tilde{C}_\xi$ and $\tilde{C}_\eta$. At this point, instead of the variables $\nu = 2n_\xi+m+1$ and $\nu' = 2K_a+m+1$, it is more convenient to introduce

$$N \equiv N_a = n_\xi+n_\eta+m+1 = \tfrac{1}{2}(\nu+\nu'), \tag{120}$$

$$\Delta = n_\xi-n_\eta = N_a-2K_a-m-1 = \tfrac{1}{2}(\nu-\nu'). \tag{121}$$

Giving just the first few terms to illustrate the procedure,

$$
\begin{aligned}
0 = \tilde{C}_\xi-\tilde{C}_\eta = {}& 4p\left\{\left(\frac{R}{2p}\right)Z_a-N\right\}+2\left\{(\Delta Z_a+NZ_b)\left(\frac{R}{2p}\right)-\Delta N\right\}\\
&+\frac{1}{4p}\left\{N^3+3N\Delta^2+N(1-m^2)-\left(\frac{R}{2p}\right)(Z_a(3N^2+3\Delta^2+1-m^2)+6N\Delta Z_b)\right.\\
&\left.+2\left(\frac{R}{2p}\right)^2(N(Z_a^2+Z_b^2)+2\Delta Z_aZ_b)\right\}+\ldots.
\end{aligned}
\tag{122}
$$

We now want to solve this equation for p as a power series in $1/R$,

$$\frac{2p}{R} = p_0+\frac{p_1}{R}+\frac{p_2}{R^2}+\ldots, \tag{123}$$

which we then square to get the desired expansion of W. However, direct substitution of this expansion into (122) would require the inversion of powers of $(R/2p)$ and $1/p$ into series in $1/R$, and would lead to such a huge number of intermediate terms that the computer calculation would become prohibitively complicated and expensive. It is much better to first expand

$$\frac{R}{2p} = r_0+\frac{r_1}{p}+\frac{r_2}{p^2}+\ldots. \tag{124}$$

When this is substituted into (122), we can easily group terms according to their order in p. We in turn equate the terms of $O(p^1)$, $O(p^0)$, $O(1/p)$, ... to zero and solve for the coefficients in (124), getting

$$r_0 = \frac{N}{Z_a}, \quad r_1 = -\frac{N^2 Z_b}{2Z_a}, \quad r_2 = \left(3\Delta + \frac{NZ_b}{Z_a}\right)\frac{N^2 Z_b}{8Z_a^2}, \ldots. \tag{125}$$

Now, the algebra required to invert (124) into (123) is not too difficult, and we obtain

$$\begin{aligned}
p = {} & \tfrac{1}{2}\tau + \tfrac{1}{2}\lambda - \lambda\{3\Delta + \lambda\}/4\tau + \lambda\{6\Delta^2 + 1 - N^2 + 3\Delta\lambda + \lambda^2\}/4\tau^2 \\
& + \lambda\{\Delta(39N^2 - 109\Delta^2 - 59 + 9m^2) + \lambda(25N^2 - 69\Delta^2 + 11 - 9m^2) + 36\lambda^2\Delta + 10\lambda^3\}/32\tau^3 \\
& + \lambda\{1065\Delta^4 - 594N^2\Delta^2 + 1203\Delta^2 - 234m^2\Delta^2 + 9m^4 + 33N^4 - 18N^2m^2 - 18m^2 - 105 - 138N^2 \\
& + 4\lambda\Delta(54m^2 + 202\Delta^2 - 162N^2 - 118) + 4\lambda^2(129\Delta^2 - 29N^2 - 7 + 9m^2) + 240\lambda^3\Delta + 56\lambda^4\}/128\tau^4 \\
& - \lambda\{\Delta(2727\Delta^4 - 2076N^2\Delta^2 + 5544\Delta^2 - 1056\Delta^2m^2 + 93m^4 + 273N^4 - 78N^2m^2 - 450m^2 \\
& + 1533 - 1470N^2) + \lambda(2421\Delta^4 - 3012N^2\Delta^2 - 3192\Delta^2 + 864\Delta^2m^2 - 70N^2 - 629 + 306m^2 \\
& - 102N^2m^2 + 219N^4 - 21m^4) + \lambda^2\Delta(1722\Delta^2 - 786N^2 - 138 + 318m^2) \\
& + \lambda^3(1038\Delta^2 - 182N^2 - 34 + 54m^2) + 420\lambda^4\Delta + 84\lambda^5\}/128\tau^5 \\
& + O(1/R^6),
\end{aligned} \tag{126}$$

where I have used the abbreviations

$$\tau = RZ_a/N, \quad \lambda = NZ_b/Z_a. \tag{127}$$

Finally, squaring (126),

$$\begin{aligned}
W = {} & -(Z_a^2/N^2)\,[\tfrac{1}{2} + \lambda/\tau - \tfrac{3}{2}\lambda\Delta/\tau^2 + \lambda(6\Delta^2 + 1 - N^2)/2\tau^3 \\
& + \{\lambda\Delta(39N^2 + 9m^2 - 59 - 109\Delta^2) + \lambda^2(17N^2 + 19 - 9m^2 - 3\Delta^2)\}/16\tau^4 \\
& + \{\lambda(1065\Delta^4 - 594N^2\Delta^2 + 1230\Delta^2 - 234m^2\Delta^2 + 9m^4 + 33N^4 - 18N^2m^2 \\
& - 18m^2 + 105 - 138N^2)/64 + \lambda^2\Delta(21\Delta^2 - 111N^2 + 63m^2 - 189)/16\}/\tau^5 \\
& + \{\lambda\Delta(-2727\Delta^4 + 2076N^2\Delta^2 - 5544\Delta^2 + 1056\Delta^2m^2 - 93m^4 - 273N^4 \\
& + 78N^2m^2 + 450m^2 - 1533 + 1470N^2)/64 + \lambda^2(-207\Delta^4 + 1044N^2\Delta^2 \\
& + 2436\Delta^2 - 576\Delta^2m^2 - 42N^2 + 371 - 162m^2 + 42N^2m^2 - 89N^4 + 15m^4)/32 \\
& + \lambda^3\Delta(3\Delta^2 - 69N^2 - 117 - 33m^2)/32\}/\tau^6 \\
& + O(1/R^7)].
\end{aligned} \tag{128}$$

The expansions for a s.a. state on centre b are obtained from the above results by interchanging the indices $_a$ and $_b$ (the index $_a$ was implicit on Δ and N). For a homonuclear o.e.d.m., we set $Z_a = Z_b$ in these formulae. Then, ignoring terms *ca.* $\exp(-4p)$, a g – u pair such as $1s\sigma_g - 2p\sigma_u$ has their energies split equally about the average given by (128), with the splitting *ca.* $\exp(-2p)$.

Comments

I have compared expansion (128) for $W(R)$ with the perturbation results of Dalgarno *et al.* and Robinson for the four s.a. states with $N = 1$ and 2, and found agreement. With $Z_b/Z_a = \lambda/N$ as the perturbation parameter, the individual contributions to W from the zeroth- to third-order energies are readily extracted from (128). From (126), we see that the sixth-order energy contributes to the terms of $O(1/R^6)$ in (p/R). When we square this to find W, the fourth- to sixth-order terms all cancel through $O(1/R^6)$. This is an example of the well-known result that if the wavefunction is in error by a term of $O(\lambda)$, the error in the energy is $O(\lambda^2)$, whereas most properties are in error by a term of $O(\lambda)$.

Komarov & Slavyanov (1968) derived this $W(R)$ expansion through $O(1/R^4)$. They did not give the expansion for p for heteronuclear o.e.d.ms, but their result for the homonuclear case (Komarov & Slavyanov 1967), given through $O(1/R^2)$, agrees to this order with (126) if we correct an apparent misprint in their equation (32), replacing 'R^3' by '$2R^3$'.

The crucial step in obtaining our general expansions of p and W is getting the expansions of C in powers of $1/p$ for the inner and outer equations. The subsequent steps are algebraic and straightforward, albeit tedious. The procedure which I have followed in getting the C expansions is itself a well-defined sequence of individually simple algebraic operations. One can thus easily program a computer to evaluate these expansions†, and this enabled me to extend the expansions of C, p and W to several orders higher than previously known. It would of course be possible to extend these results even further using this approach.

These expansions are asymptotic series, but they can be very accurate for R 'large enough'. In our derivation, we assumed that $R \gg 2N_a/Z_a$ so that p would be large, but this is much too vague and does not furnish us with a practical estimate of the required magnitude of R. Ponomarev & Puzynina (1967) have shown that some simple physical reasoning both gives one an estimate of the size of R required and rationalizes why the large R expansion can succeed in the first place. We initially treat the electron as a classical particle, moving in the two three-dimensional potential wells from the term $-Z_a/r_a - Z_a/r_b$ in the Hamiltonian. The potential barrier between these two wells has its minimum along the line joining the nuclei, a distance

$$R/\{1+\sqrt{(Z_b/Z_a)}\}$$

from centre a, with

$$U_{max}(R) = -(\sqrt{Z_a}+\sqrt{Z_b})^2/R. \tag{129}$$

When $W < U_{max}$, the classical electron is trapped in either well a or well b. For $0 > W > U_{max}$, the electron is still bound, but moves back and forth between both centres. When we take quantum mechanics into account, the allowed energy levels in each well are discrete, and the electron can tunnel from one well to the other. However, if R is large so that the barrier is wide, the electron may still be effectively trapped in one of the wells when $W < U_{max}$.

Our derivation of the expansion for $Y(\eta)$ assumed that the electron was localized on centre a. This enabled us to derive formulae using the centre a s.a. quantum numbers, (26), and this ignores any nodes in $Y(\eta)$ near centre b. Clearly, we must have $W < U_{max}$ in order for the large R expansions to be applicable. Using just the first two terms in (128) to approximate W, we find that $W < U_{max}$ for $R > R_x$, where

$$R_x \simeq 2N_a^2\{Z_a + 2\sqrt{(Z_a Z_b)}\}/Z_a^2. \tag{130}$$

Keeping additional terms in the expansion for W makes only a slight change in this estimate for R_x. The actual accuracy of the expansion will vary from case to case; one can get an estimate of the accuracy with which (128) gives W by comparing the magnitudes of successive terms.

Splittings between energy levels: quasi-crossings of potential curves

Our assumption that the electron is trapped in one well if $W < U_{max}$ breaks down if there is a degenerate energy level in the second well and both states have the same nodal quantum numbers n_ξ and n_ϕ. This degeneracy occurs by symmetry for homonuclear o.e.d.ms and by 'accident'

† Barton & Fitch (1972) give many examples of the rapidly increasing usage of computers to do algebra.

for heteronuclear o.e.d.ms. In such a situation, the electron has a much larger probability of tunnelling from one well to the other as compared to the non-degenerate case, and since the electron can occupy allowed energy levels in both wells, it is shared by both. The energy levels in the two wells will interact and split, so in speaking of degeneracy, we will mean prior to taking this interaction into account.

The accidental degeneracy in the heteronuclear case is especially interesting because it results in *quasi-crossings* of potential curves, a phenomenon first noted by Ponomarev & Puzynina (1967) in their extensive numerical calculations. When $Z_a \neq Z_b$ and we ignore the interaction between eigenstates in the two wells, the energy levels in the two wells move relative to one another as R is varied, and can even cross. Consider a state with the electron localized in well b when R is

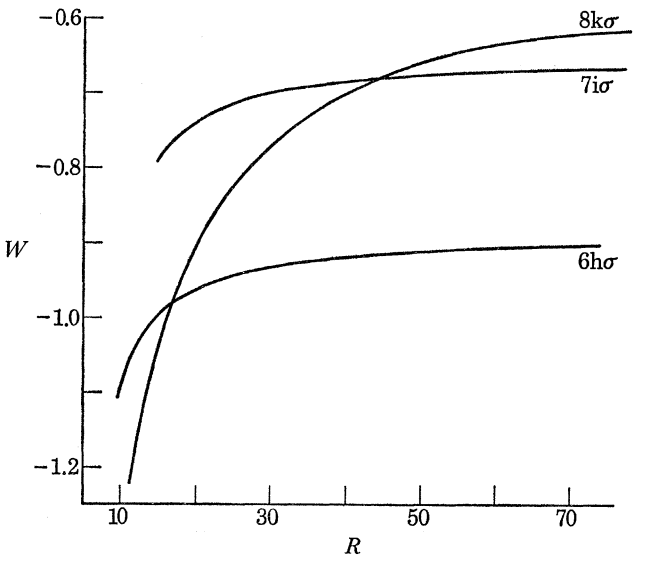

FIGURE 1. Quasi-crossings of the potential curves of the 6hσ, 7iσ and 8kσ states of OH^{8+}. Electronic energy W against distance R (atomic units).

very large, and suppose that as we decrease R, we reach the point R_q where this state is degenerate with one in well a having the same n_ξ and n_ϕ and that for $R < R_q$ this latter state is higher in energy than is the eigenstate in well b. A crossing of the exact levels would contradict the o.e.d.m. non-crossing rule, so when we take the interaction between the states into account, we find that the electron is shared by both wells at $R = R_q$ and then localized in well a for $R < R_q$. As R decreases through R_q, the electron moves from well b to well a, so the quasi-crossing of potential curves plays a very important role in charge transfer in atomic collisions.

Our derivation of the $1/R$ expansion of W ignored all interaction with states of the second well, so the potential curves calculated using (128) can cross. Figure 1 depicts two quasi-crossings in OH^{8+}. The 6hσ and 7iσ states both dissociate into $O^{7+} + H^+$, with s.a. quantum numbers $N, K, m = 6, 5, 0$ and $7, 6, 0$. The 8kσ state dissociates into $O^{8+} + H$ in its ground state. Using (128) to calculate the potential curves, we find that of the 8kσ state crosses the 7iσ curve near $R = 44$ bohr and the 6hσ curve near 17 bohr. The exact potential curves have avoided crossings. The 8kσ curve from (128) is valid down to $R_x \simeq 13$ bohr, but for $13 < R < 17$ it corresponds to the exact 6hσ curve, and for $17 < R < 44$, the exact 7iσ curve. Only for $R > 44$ does it describe the exact 8kσ curve. Incidentally, the 8kσ and 5gσ curves from (128) intersect near $R = 8.5$ bohr,

but this is well below the R_x values for these two states and thus meaningless. Figure 2 shows the crossing of the $1/R$ curves and avoided crossing of the exact curves for the 4fσ and 5gσ states of BH^{5+}.

We can calculate the exponentially small splittings, between the g – u pairs for homonuclear o.e.d.ms and quasi-crossing states of heteronuclear o.e.d.ms by evaluating the exponentially small δn_η which we earlier ignored in finding the $1/R$ expansions. We have two distinct expansions for $Y(\eta)$ for a heteronuclear o.e.d.m., Y_- for $\eta \leqslant 0$ and Y_+ for $\eta \geqslant 0$. Matching up these functions and their derivatives at $\eta = 0$ gives

$$\left(Y_- \frac{dY_+}{d\eta} - Y_+ \frac{dY_-}{d\eta}\right)_{\eta=0} = 0, \tag{131}$$

and we need a non-zero δn_η in order to satisfy this boundary condition. There has been some confusion about the homonuclear boundary conditions. For a homonuclear o.e.d.m. we have $Y_+(\eta) = \pm Y_-(-\eta)$, and will drop the + and − subscripts. The total homonuclear wavefunction

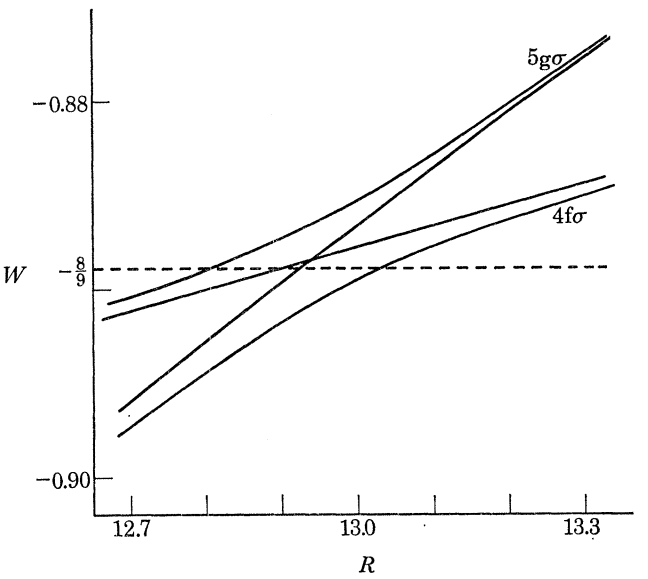

FIGURE 2. Quasi-crossing of the potential curves for the 4fσ and 5gσ states of BH^{5+}. The $(1/R)$ series approximate curves cross, the exact curves have an avoided crossing.

is either even or odd with respect to inversion through the molecular mid-point. Inversion takes (ξ, η, ϕ) into $(\xi, -\eta, \phi \pm \pi)$. The $\exp(\pm im\phi)$ gives a factor of $(-1)^m$ when inverted, so we must have $Y(-\eta) = (-1)^m Y(\eta)$ for a g state and $(-1)^{m+1} Y(\eta)$ for a u state. To get $Y(\eta)$ an even function, we require that

$$dY(0)/d\eta = 0, \tag{132}$$

and for $Y(\eta)$ odd,

$$Y(0) = 0. \tag{133}$$

Komarov & Slavyanov (1967) ignored the factor of $(-1)^m$ and used these boundary conditions for g and u states, respectively, so their final equation for the energy splitting between g and u states should be multiplied by $(-1)^m$.

Let us denote the value of δn_η found from (132) as δn_g and that from (133) as δn_u, so the g–u

subscripts here denote the parity of $Y(\eta)$. Komarov & Slavyanov found that $\delta n_g = -\delta n_u$ to the order to which they evaluated these terms, but were unable to prove this result in general. I offer the following proof. We suppress the other parameters, which are irrelevant, and write $Y = Y(\eta, n)$, where n is either n_g or n_u. By assumption,

$$n_g = K + \delta n_g, \quad n_u = K + \delta n_u, \tag{134}$$

where δn_g and δn_u are both small and K is the s.a. parabolic quantum number, which gives the number of nodes in Y in one of the wells. From the use of Taylor series expansions, the boundary conditions (132) and (133) give

$$\left.\frac{\partial Y}{\partial \eta}\right|_{0,\, n_g} = \left.\frac{\partial Y}{\partial \eta}\right|_{0,\, K} + \delta n_g \left.\frac{\partial^2 Y}{\partial n\, \partial \eta}\right|_{0,\, K} + \ldots = 0, \tag{135}$$

$$Y(0, n_u) = Y(0, K) + \delta n_u \left.\frac{\partial Y}{\partial n}\right|_{0,\, K} + \ldots = 0. \tag{136}$$

Solving for δn_g and δn_u,

$$\delta n_g = -\frac{\partial Y}{\partial \eta} \Big/ \left.\frac{\partial^2 Y}{\partial n\, \partial \eta}\right|_{0,\, K}, \tag{137}$$

$$\delta n_u = -Y \Big/ \left.\frac{\partial Y}{\partial n}\right|_{0,\, K}. \tag{138}$$

Consider

$$\frac{\partial}{\partial n} Y^2(\eta, n) = 2Y(\eta, n) \frac{\partial Y(\eta, n)}{\partial \eta}, \tag{139}$$

which is zero at $\eta = 0$ when $n = n_g$ or n_u. Again making Taylor series expansions,

$$\left.\frac{\partial}{\partial \eta} Y^2\right|_{0,\, n_u} = \left.\frac{\partial}{\partial \eta} Y^2\right|_{0,\, K} + \delta n_u \left.\frac{\partial^2 Y^2}{\partial n\, \partial \eta}\right|_{0,\, K} + \ldots = 0, \tag{140}$$

$$\left.\frac{\partial}{\partial \eta} Y^2\right|_{0,\, n_g} = \left.\frac{\partial}{\partial \eta} Y^2\right|_{0,\, K} + \delta n_g \left.\frac{\partial^2 Y^2}{\partial n\, \partial \eta}\right|_{0,\, K} + \ldots = 0. \tag{141}$$

Subtracting, we get

$$(\delta n_u - \delta n_g) \left.\frac{\partial^2 Y^2}{\partial n\, \partial \eta}\right|_{0,\, K} = 0. \tag{142}$$

We know from the results of previous workers, and could show by several alternative arguments, that $\delta n_g \neq \delta n_u$, so we must have

$$\left.\frac{\partial^2 Y^2}{\partial n\, \partial \eta}\right|_{0,\, K} = 2\left(Y \frac{\partial^2 Y}{\partial n\, \partial \eta} + \frac{\partial Y}{\partial n} \frac{\partial Y}{\partial \eta}\right)_{0,\, K} = 0. \tag{143}$$

Dividing this by $(\partial Y/\partial \eta)\,(\partial^2 Y/\partial n\, \partial \eta)$ and comparing the results with (137) and (138) proves that $\delta n_g = -\delta n_u$. We were justified in truncating all of these Taylor series expansions after just two terms because the terms of $O(\delta n_\eta^2)$ are exponentially smaller than those we retained, and give corrections to δn_η of

$$O\,(\exp\,(-4p)),$$

which we are ignoring.

The series expansions which we used for $X(\xi)$ and $Y(\eta)$ led to a scheme for evaluating C/p as a power series in $1/p$ which is, I believe, much easier to carry through than are the alternative approaches which other workers have used. However, when it comes to determining δn_η from the boundary conditions, the series expansion becomes quite cumbersome. Still, it is very

instructive to work through and find the lead term of δn_η for a particular case, a homonuclear o.e.d.m. using boundary condition (133). We set $D = 0$ and drop the $+$ and $-$ subscripts on Λ, and (133) then gives $\Lambda(2p) = 0$, which we want to solve for δn_u. Using (87) and (138), we have

$$\delta n_u = -\sum_{j=0}^{\infty} h_j M(-j, m+1, 2p) \Big/ \sum_{j=0}^{\infty} h_j \frac{\partial}{\partial j} M(-j, m+1, 2p). \tag{144}$$

In keeping with the spirit of the asymptotic expansions, we assume that p is very large and ignore the fact that the summation index j must eventually surpass p, that is, $p \gg j$. Using (75), we keep only the dominant terms and make the approximations

$$M(-j, m+1, 2p) \simeq m!(-2p)^j/(j+m)!, \tag{145}$$

$$\partial M(-j, m+1, 2p)/\partial j \simeq m! j!(-1)^{j+1} \exp(2p)/(2p)^{j+m+1}. \tag{146}$$

We also make the approximations

$$h_{j+1}/h_j \simeq -\alpha_{j+1}/\beta_{j+1} \simeq -(j+m+1)^2/4p(j+1-K) \quad (j \geqslant K), \tag{147}$$

$$h_{j-1}/h_j \simeq -\gamma_{j-1}/\beta_{j-1} \simeq j^2/4p(K+1-j) \quad (j \leqslant K). \tag{148}$$

Neither numerator nor denominator in (144) are dominated by the single term with $j = K$. In the numerator, the factor $1/p$ from h_{K+1}/h_K is cancelled by the one higher power of p from $M(-(K+1), m+1, 2p)$, so the term with $j = K+1$ is of the same magnitude as the term with $j = K$. Keeping only the lead terms, the sum in the numerator is from $j = K$ to infinity, and the denominator from $j = 0$ to K. The numerator gives

$$\frac{h_K(-2p)^K}{(K+m)!}\left(1-\left(\frac{h_{K+1}}{h_K}\right)\frac{2p}{K+m+1}\left(1-\left(\frac{h_{K+2}}{h_{K+1}}\right)\frac{2p}{K+m+2}(1-\ldots)\right)\right)$$
$$= \frac{h_K(-2p)^K}{(K+m)!}\left(1+\frac{K+m+1}{2}\left(1+\frac{K+m+2}{4}\left(1+\frac{K+m+3}{6}(1+\ldots)\right)\right)\right). \tag{149}$$

The denominator is evaluated similarly, and we find

$$\delta n_u \simeq \frac{(2p)^{2K+m+1}\,e^{-2p}}{K!\,(K+m)!}\sum_{j=0}^{\infty}\binom{K+m+j}{j}\frac{1}{2^j}\Big/\sum_{j=0}^{K}\binom{K}{j}\frac{1}{(-2)^j}. \tag{150}$$

We recognize these two summations as respectively $(1-\frac{1}{2})^{-(K+m+1)} = 2^{K+m+1}$ and $(1-\frac{1}{2})^K = 2^{-K}$, so

$$\delta n_u \simeq (4p)^{2K+m+1}\,e^{-2p}/K!(K+m)!, \tag{151}$$

in agreement with the results of previous workers. Note that if we only used the single term $j = K$ in the summations, the result would be off by the factor 2^{2K+m+1}.

This calculation demonstrates that the single term with $j = K$ does not necessarily give the dominant contribution to $Y(\eta)$ away from $\eta = \pm 1$. Similar results will certainly hold in the heteronuclear case. It is thus non-trivial to prove that the higher order corrections do not change the number of nodes of the limiting s.a. wavefunctions used by Morse & Stueckelberg and Gershtein & Krivchenkov in correlating u.a. and s.a. states.

The splitting between g and u states of homonuclear o.e.d.ms has been evaluated by Herring (1962), Landau & Lifshitz (1965), Smirnov (1964), Ovchinnikov & Sukhanov (1964), Gershtein *et al.* (1965), Komarov & Slavyanov (1967), and Damburg & Propin (1968). For heteronuclear o.e.d.ms the splitting at a quasi-crossing has been estimated by Ponomarev (1968) and Komarov & Slavyanov (1968). These authors agreed that the quasi-crossings occur at points where

$$W = -(Z_a - Z_b)^2/2(K_a - K_b)^2, \tag{152}$$

but their estimates for the splitting disagree. Using the J.W.K.B. method, Ponomarev found

$$\delta W = -4W(4p)^{K_a+K_b+1}e^{-2p}/K_a!\,K_b!\sqrt{(N_a N_b)} \tag{153}$$

for σ states, whereas Komarov & Slavyanov found the general result

$$\delta W = \frac{-4W(4p)^{K_a+K_b+m+1}e^{-2p}}{(K_a-K_b)\{K_a!\,K_b!(K_a+m)!\,(K_b+m)!\}^{\frac{1}{2}}} \times\left\{1-\frac{1}{4p}(K_a^2+K_b^2+4K_aK_b+(m+1)(3K_a+3K_b+m+2))+\ldots\right\}, \tag{154}$$

the lead term of which does not reduce to (153) when $m = 0$. Both tested their results only for the splitting between the 4fσ and 5gσ states of BH^{5+}. Although the value given by (154) is quite accurate in this case, the second term in (154) is about $-60\,\%$ the size of the lead term. This is much too large to confidently truncate the expansion with just two terms, so besides attempting to resolve the discrepancy between (153) and (154), I shall also extend the order of the results.

The modified comparison method (Slavyanov 1967), used by Komarov & Slavyanov, seems to be the most suitable approach for simultaneously finding δn_η for homonuclear and heteronuclear o.e.d.ms. Treating both cases simultaneously will make clear their similarities and differences. For η near -1, we use a solution of the form

$$Y_-(\eta) = M_{\chi,\frac{1}{2}m}(2pt(\eta))/\sqrt{\{t'(\eta)\,(1-\eta^2)\}}, \tag{155}$$

where $M_{\chi,\frac{1}{2}m}$ is the Whittaker function (Abramowitz & Stegun),

$$M_{\chi,\frac{1}{2}m}(y) = e^{-\frac{1}{2}y}y^{\frac{1}{2}(m+1)}M(\tfrac{1}{2}(m+1)-\chi, m+1, y), \tag{156}$$

$$\left(\frac{d^2}{dy^2}-\frac{1}{4}+\frac{\chi}{y}+\frac{1-m^2}{4y^2}\right)M_\chi(y)_{\frac{1}{2}m} = 0. \tag{157}$$

This gives an equation for $t(\eta)$,

$$\left\{(t')^2-1+\frac{2}{p}\left(\frac{(C/2p-D\eta)}{(1-\eta^2)}-\frac{\chi(t')^2}{t}\right)+\frac{1-m^2}{4p^2}\left(\frac{4}{(1-\eta^2)^2}-\left(\frac{t'}{t}\right)^2\right)-\frac{1}{2p^2}\left(\frac{t'''}{t'}-\frac{3}{2}\left(\frac{t''}{t'}\right)^2\right)\right\} = 0, \tag{158}$$

where a prime denotes differentiation with respect to η. For a centre a s.a. state, comparison with our previous results shows that as $R \to \infty$ we must have $t(\eta) \simeq 1+\eta$ and

$$\chi = K_a+\tfrac{1}{2}(m+1)+\delta n_\eta. \tag{159}$$

The inner equation has regular singular points at $\eta = \pm 1$. For the solution used near $\eta = -1$ requiring that the regular singular point at $\eta = -1$ remains a regular singular point in the transformed equations gives the condition

$$t(-1) = 0. \tag{160}$$

Then, in order not to have divergences in (158) at $\eta = -1$, we must have

$$C/p = -2D+4\chi t'(-1)+\frac{1-m^2}{2p}(t''(-1)/t'(-1)-1), \tag{161}$$

which is used to get the expansion of C/p.

We now solve for t and C/p by expanding them as power series in $1/p$, grouping terms according to their order in p, and solving successively for each order. I find

$$t(\eta) = \{1+\eta\} + \frac{1}{p}\left\{(\chi-D)\ln\left(\frac{1-\eta}{2}\right)\right\} + \frac{1}{p^2}\left\{\frac{\chi(\chi-D)}{1+\eta}\ln\left(\frac{1-\eta}{2}\right) - \frac{(\chi-D)^2+\omega}{2(1-\eta)}\right.$$
$$\left. + \tfrac{1}{4}((\chi-D)^2+\omega) + \tfrac{1}{2}\chi(\chi-D)\right\} + \frac{1}{p^3}\left\{-\frac{\chi(\chi-D)^2}{(1+\eta)^2}\ln^2\left(\frac{1-\eta}{2}\right) + \frac{(3\chi^2+\omega)(\chi-D)}{2(1+\eta)^2}\ln\left(\frac{1-\eta}{2}\right)\right.$$
$$- \frac{\chi((\chi-D)^2+\omega)}{2(1-\eta)} - \frac{(\chi-D)((\chi-D)^2+\omega+1)}{4(1-\eta)^2} + \frac{(3\chi^2+\omega)(\chi-D)}{4(1+\eta)}$$
$$\left. + \tfrac{1}{16}(10\chi^3 - 18\chi^2 D + 9\chi D^2 - 2\omega D - D^3 + 6\omega\chi + \chi - D)\right\} + \ldots, \tag{162}$$

where
$$\omega = \tfrac{1}{4}(1-m^2) \tag{163}$$

Komarov & Slavyanov derived this general expansion through $O(1/p^2)$, and the homonuclear expansion (simply set $D = 0$ in (162)) through $O(1/p^3)$. We can use (162) in (161) to find through $O(1/p^2)$ the expansion $\tilde{C}_\eta$ analogous to (119) for $\tilde{C}_\xi$. Komarov & Slavyanov were able to get $\tilde{C}_\eta$ through $O(1/p^3)$ by finding the first few terms in Taylor series expansions about $\eta = -1$ of the $1/p^3$ and $1/p^4$ terms of $t(\eta)$.

To get $Y_+(\eta)$, used near $\eta = +1$, we simply make the replacements

$$\chi \to \chi', \quad \eta \to -\eta, \quad D \to -D \tag{164}$$

in $Y_-(\eta)$. χ' is a new index, which we shall relate to χ. Using Y_- in (161) gives

$$\tilde{C}_\eta = 2p(2\chi - D) - 2(\chi^2+\omega-\chi D) - (1/2p)(2\chi(\chi^2+\omega) - (3\chi^2+\omega)D + \chi D^2) + \ldots, \tag{165}$$

whereas using Y_+ in its analogous equation gives

$$\tilde{C}_\eta = 2p(2\chi' + D) - 2(\chi'^2+\omega+\chi' D) - (1/2p)(2\chi'(\chi'^2+\omega) + (3\chi'^2+\omega)D + \chi' D^2) + \ldots. \tag{166}$$

Since these two expansions must be equal, we can express χ' in terms of χ, D, m and p. Equating terms of $O(p)$ gives

$$\chi - \chi' = D, \tag{167}$$

and this also makes equal the next few orders in (165) and (166). However, this does not rule out the possibility that (167) is accurate only to $O(1/p^j)$ for some j. Komarov & Slavyanov (1969) showed that (167) is exact for the special case $Z_b = 0$. One can easily show that if (167) holds then the elements of the continued fraction (92) are symmetric with respect to χ and χ', so we conclude that (167) is exact. In the homonuclear case, we must have $\chi' = \chi$ by symmetry; this is consistent with (167).

In order for $Y_+(\eta)$ to reduce to the η-part of Ψ^b as $R \to \infty$, we must have

$$\chi' = K_b + \tfrac{1}{2}(m+1) + \delta n_\eta. \tag{168}$$

To have quasi-crossing, we need degenerate levels in the two wells. χ must be of the form (159) to have an allowed level in well a, and χ' of the form (168) for well b. In general, we will not have both satisfied simultaneously; when they are, (167) gives

$$D = K_a - K_b = \text{integer}, \tag{169}$$

and this in turn gives (152) for the energy at the point of quasi-crossing. In the homonuclear case, (169) is satisfied for all R.

In deriving the $1/R$ expansions of W, we essentially assume that there is no overlap between Ψ^{a} describing an eigenstate of well a and Ψ^{b} of well b. When Ψ^{a} and Ψ^{b} are degenerate, the electron is shared by both wells, and we must express the wave function as a linear combination of Ψ^{a} and Ψ^{b}. If there is no overlap between Ψ^{a} and Ψ^{b}, this linear combination must be

$$\Psi_{\pm} = \Psi^{\mathrm{a}} \pm \Psi^{\mathrm{b}} \tag{170}$$

in order to have the two degenerate wavefunctions orthogonal. We previously argued that the homonuclear wavefunctions must be of the form (170) by symmetry. Continuing to ignore overlap between Ψ^{a} and Ψ^{b}, the energy for $\Psi_{\pm}$ is the average of (128) and its centre b analogue, giving

$$W = \frac{1}{2}\left\{-\frac{Z_{\mathrm{a}}^2}{2N_{\mathrm{a}}^2} - \frac{Z_{\mathrm{b}}}{R} + \frac{3N_{\mathrm{a}}\Delta_{\mathrm{a}}Z_{\mathrm{b}}}{2Z_{\mathrm{a}}R^2} + \ldots - \frac{Z_{\mathrm{b}}^2}{2N_{\mathrm{b}}^2} - \frac{Z_{\mathrm{a}}}{R} + \frac{3N_{\mathrm{b}}\Delta_{\mathrm{b}}Z_{\mathrm{a}}}{2Z_{\mathrm{b}}R^2} + \ldots\right\}. \tag{171}$$

(If the asymptotic series were exact, both terms in (171) would give the same numerical value at R_{q}.) When $Z_{\mathrm{a}} = Z_{\mathrm{b}}$, the terms in (171) are identical.

The energy is equal to (152) at the point of quasi-crossing, so we equate (171) to (152) and solve for R_{q}. Keeping just the terms through $O(1/R)$ in (171) gives the starting estimate

$$R_{\mathrm{q}}^{(0)} = (Z_{\mathrm{a}} + Z_{\mathrm{b}})\left\{\frac{(Z_{\mathrm{a}} - Z_{\mathrm{b}})^2}{(K_{\mathrm{a}} - K_{\mathrm{b}})^2} - \frac{1}{2}\left(\frac{Z_{\mathrm{a}}^2}{N_{\mathrm{a}}^2} + \frac{Z_{\mathrm{b}}^2}{N_{\mathrm{b}}^2}\right)\right\}^{-1}. \tag{172}$$

We then improve this initial guess by using the iteration function

$$R_{\mathrm{q}}^{(i+1)} = \left\{\frac{(Z_{\mathrm{a}} - Z_{\mathrm{b}})^2}{(K_{\mathrm{a}} - K_{\mathrm{b}})^2} - \frac{1}{2}\left(\frac{Z_{\mathrm{a}}^2}{N_{\mathrm{a}}^2} + \frac{Z_{\mathrm{b}}^2}{N_{\mathrm{b}}^2}\right)\right\}^{-1}\left\{Z_{\mathrm{a}} + Z_{\mathrm{b}} - 3\left(\frac{N_{\mathrm{a}}\Delta_{\mathrm{a}}Z_{\mathrm{b}}}{Z_{\mathrm{a}}} + \frac{N_{\mathrm{b}}\Delta_{\mathrm{b}}Z_{\mathrm{a}}}{Z_{\mathrm{b}}}\right)\Big/ 2R_{\mathrm{q}}^{(i)} + \ldots\right\}. \tag{173}$$

We find $R_q = 16.71$ and 44.31 for the two quasi-crossings of OH^{8+} shown in figure 1, and $R_{\mathrm{q}} = 12.92$ for the BH^{5+} quasi-crossing in figure 2. Note that the two curves in figure 2 do not intersect at exactly $W = -\frac{8}{9}$. Evaluating additional terms beyond $O(1/R^6)$ would possibly improve the agreement between the actual and predicted intersection points, but because the series are asymptotic, the agreement also could worsen. The minimum splitting between the two exact curves in figure 2 is at $R = 12.96$, so there is a slight ambiguity in defining the 'point' of quasi-crossing.

We will now evaluate δn_η, and then the splitting. Let us denote the dependence of $t(\eta)$ on the remaining parameters as $t(\eta; p, \chi, D)$. The replacements

$$p \to -p, \quad \chi \to -\chi, \quad D \to -D \tag{174}$$

cause the changes

$$\beta_{i+k} \to \beta_{i-k}, \quad \alpha_{i+k} \to \gamma_{i-k}, \quad \gamma_{i+k} \to \alpha_{i-k} \tag{175}$$

in the continued fraction (92). Since our expansion of (92) treated the finite and infinite continued fractions exactly the same, (175) makes no change in our expansion, hence $\tilde{C}_\eta$ is invariant to (174). It then follows from (158) that

$$t(\eta; p, \chi, D) = t(\eta; -p, -\chi, -D). \tag{176}$$

We define

$$G(\eta; p, \chi, D) = \frac{m!(-2pt(\eta; p, \chi, D))^{\chi}\exp(-pt(\eta; p, \chi, D))}{\Gamma(\frac{1}{2}(m+1)+\chi)\,(t'(\eta; p, \chi, D))^{\frac{1}{2}}} \times\left\{\sum_{j=0}^{J}\frac{(\frac{1}{2}(m+1)-\chi)_j\,(\frac{1}{2}(1-m)-\chi)_j}{j!\,(-2pt(\eta; p, \chi, D))^j} + O(|1/t|^{J+1})\right\}, \tag{177}$$

and use (69), (155), (156) and (176) to obtain

$$Y_-(\eta) = (1-\eta^2)^{-\frac{1}{2}}\{(-1)^{-\frac{1}{2}(m+1)}G(\eta;p,\chi,D)+G(\eta;-p,-\chi,-D)\}, \tag{178}$$

which is valid in the asymptotic region near $\eta = 0$. Using (164) to get Y_+ from Y_-, we have

$$Y_+(\eta) = (1-\eta^2)^{-\frac{1}{2}}\{(-1)^{-\frac{1}{2}(m+1)}G(-\eta;p,\chi',-D)+G(-\eta;-p,-\chi',D)\}. \tag{179}$$

Using (162) for t in (177), after considerable algebra I find

$$\begin{aligned}G(\eta;p,\chi,D) = {}& \frac{m!}{\Gamma(\frac{1}{2}(m+1)+\chi)}(-2p(1+\eta))^{\chi}(2/(1+\eta))^{\chi-D}\mathrm{e}^{-p(1+\eta)}\\
&\times\{1+(1/p)\{(\chi^2+\chi+\omega-D(1+2\chi)+D^2)/2(1-\eta)-(\chi^2-\chi+\omega)/2(1+\eta)\\
&-\tfrac{1}{4}(3\chi^2+\omega-4\chi D+D^2)\}\\
&+(1/p^2)\{(-4\chi^4-\chi^3+3\chi^2-6\chi^2\omega+\chi\omega-2\omega^2+D(12\chi^3+2\chi^2+8\chi\omega\\
&+2\omega-3\chi)-D^2(13\chi^2+2\chi+3\omega)+D^3(6\chi+1)-D^4)/8(1-\eta)\\
&+(\chi^4+4\chi^3+5\chi^2+2\chi+2\chi^2\omega+4\chi\omega+\omega^2+2\omega-D(4\chi^3+12\chi^2\\
&+10\chi+4\chi\omega+4\omega+2)+D^2(6\chi^2+12\chi+2\omega+5)\\
&-D^3(4\chi+4)+D^4)/8(1-\eta)^2\\
&+(\chi^4-4\chi^3+5\chi^2-2\chi+2\chi^2\omega-4\chi\omega+2\omega+\omega^2)/8(1+\eta)^2\\
&+(\chi-D)(2\chi^3-5\chi^2+3\chi+2\chi\omega-3\omega)/8(1+\eta)\\
&-\tfrac{1}{16}(10\chi^3-18\chi^2D+9\chi D^2-2\omega D-D^3+6\omega\chi+\chi-D)\\
&+\tfrac{1}{32}(9\chi^4+6\chi^2\omega+\omega^2-D(24\chi^3+8\chi\omega)+D^2(22\chi^2+2\omega)-8\chi D^3+D^4)\\
&+O(1/p^3)\}.\end{aligned} \tag{180}$$

This gives

$$\begin{aligned}G(0;p,\chi,D) = {}& m!(-4p)^{\chi}2^{-D}\mathrm{e}^{-p}(\Gamma(\tfrac{1}{2}(m+1)+\chi))^{-1}\\
&\times\{1+(1/4p)(-3\chi^2+4\chi-\omega-2D+D^2)+(1/32p^2)(9\chi^4-44\chi^3+64\chi^2-2\chi\\
&+6\chi^2\omega+\omega^2-20\chi\omega+16\omega+D(16\chi^2-64\chi-6+8\omega)+D^2(-6\chi^2+22\chi\\
&+20-2\omega)-10D^3+D^4)+O(1/p^3)\},\end{aligned} \tag{181}$$

$$\begin{aligned}(\partial/\partial\eta)\,G(0;p,\chi,D) = G'(0;p,\chi,D) = {}& (-p)\,m!\,(-4p)^{\chi}2^{-D}\mathrm{e}^{-p}(\Gamma(\tfrac{1}{2}(m+1)+\chi))^{-1}\\
&\times\{1+(1/4p),(-3\chi^2-4\chi-\omega+2D+D^2)+(1/32p^2)(9\chi^4+4\chi^3-32\chi^2\\
&-2\chi+6\chi^2\omega+\omega^2-4\chi\omega-16\omega+D(-8\chi^2+32\chi+10)+D^2(-6\chi^2+6\chi\\
&-12-2\omega)-2D^3+D^4)+O(1/p^3)\}.\end{aligned} \tag{182}$$

First consider the homonuclear boundary conditions. Equation (133) gives

$$(-1)^{-\frac{1}{2}(m+1)}G(0;p,\chi,0)+G(0;-p,-\chi,0) = 0. \tag{183}$$

Using (159) and (74), we have the factor

$$1/\Gamma(\tfrac{1}{2}(m+1)-\chi) \simeq K!(-1)^{K+1}\delta n_{\mathrm{u}} \tag{184}$$

from the second term, and some simple algebra then yields

$$\begin{aligned}\delta n_{\mathrm{u}} = {}& (4p)^{2K+m+1}\mathrm{e}^{-2p}(K!(K+m)!)^{-1}\{1-(1/2p)(3\chi^2+\omega)\\
&+(1/8p^2)(9\chi^4-10\chi^3+6\chi^2\omega-6\chi\omega+\omega^2-\chi)+\ldots\}.\end{aligned} \tag{185}$$

One finds that using (182) for boundary condition (132) gives $\delta n_g = -\delta n_u$, which serves as a partial check on the correctness of expansion (180). Imposition of the general boundary condition (131) leads ultimately to

$$\begin{aligned}1/(\Gamma(\tfrac{1}{2}(m+1)-\chi)\,\Gamma(\tfrac{1}{2}(m+1)-\chi')) = {} & (-1)^{\chi+\chi'-m-1}(4p)^{2(\chi+\chi')}\mathrm{e}^{-4p}\,(\Gamma(\tfrac{1}{2}(m+1)+\chi)\\ & \times\Gamma(\tfrac{1}{2}(m+1)+\chi'))^{-1}\{1-(1/2p)\,(\chi^2+\chi'^2+4\chi\chi'+2\omega)\\ & +(1/8p^2)\,((\chi^2+\chi'^2+4\chi\chi'+2\omega)^2-\chi^3-9\chi^2\chi'-9\chi\chi'^2\\ & -\chi'^3-\chi-\chi'-6\omega(\chi+\chi'))+O(1/p^3)\}. \qquad (186)\end{aligned}$$

The value of δn_η found by solving this equation depends dramatically upon the values of χ and χ'. If $Z_b = 0$, then χ is given by (159), we find $\chi - \chi' = N_a$ so that χ' is negative and (186) gives $\delta n_\eta = 0$, as expected. If χ is of the form (159) and $\frac{1}{2}(m+1) \pm \chi'$ is not too close to zero or a negative integer, we find $\delta n_\eta \sim \exp(-4p)$. We are particularly interested in the solution at a quasi-crossing, when χ and χ' are of the forms (159) and (168), respectively. Then both gamma functions on the l.h.s. of (186) give a factor of δn_η, when expanded as in (184), and we find

$$\begin{aligned}\delta n_\eta = {} & \pm(4p)^{K_a+K+m+1}\mathrm{e}^{-2p}(K_a!\,K_b!(K_a+m)!\,(K_b+m)!)^{-\frac{1}{2}}\{1-(1/4p)\,(\chi^2+\chi'^2+4\chi\chi'+2\omega)\\ & +(1/32p^2)\,((\chi^2+\chi'^2+4\chi\chi'+2\omega)^2-2(\chi^3+9\chi^2\chi'+9\chi\chi'^2+\chi'^3+\chi+\chi'\\ & +6\omega(\chi+\chi')))+\ldots\}. \qquad (187)\end{aligned}$$

When $Z_a = Z_b$, this simplifies to $\pm\delta n_u$ of (185).

We ignored δn_η when we carried out the final steps of the derivation of (128), the $1/R$ expansion of $W(R)$. Exactly the same analysis goes through if we do not ignore δn_η; we must merely replace K_a by $K_a + \delta n_\eta$ in these equations. The net result is to replace N_a by $N_a + \delta n_\eta$ and Δ_a by $\Delta_a - \delta n_\eta$ in (128); the first few terms then are

$$W^a(R) = -Z_a^2/2(N_a+\delta n_\eta)^2 - Z_b/R + 3(N_a+\delta n_\eta)\,(\Delta_a-\delta n_\eta)\,Z_b/2Z_a R^2 + \ldots. \qquad (188)$$

This shows that a negative δn_η lowers the energy and a positive δn_η increases the energy. Analogous results hold for the centre b expansion. In the homonuclear case, we must identify $\delta n_\eta = (-1)^m \delta n_u$ for the u states, which are higher in energy for m even and lower for m odd.

Expanding about $\delta n_\eta = 0$,

$$W = W|_{\delta n\eta=0} + \delta n_\eta\,\partial W/\partial\delta n_\eta|_{\delta n\eta=0} + \ldots, \qquad (189)$$

and then

$$\delta W = 2|\delta n_\eta|\,\partial W/\partial\delta n_\eta|_{\delta n\eta=0}. \qquad (190)$$

At the point of quasi-crossing, the proper energy expression is (171), the average of the centre a and b expansions. Although (almost) equal numerically, the derivatives with respect to δn_η of these two expansions are quite different. This gives

$$\begin{aligned}\delta W = {} & |\delta n_\eta|\left\{\frac{Z_a^2}{N_a^3}+\frac{Z_b^2}{N_b^3}-3\left(\frac{(N_a-\Delta_a)\,Z_b}{Z_a}+\frac{(N_a-\Delta_b)\,Z_a}{Z_b}\right)\Big/2R_q^2\right.\\ & \left.-\frac{Z_b N_a(1-4N_a^2+6\Delta_a^2-6N_a\Delta_a)}{Z_a^2R_q^3}-\frac{Z_a N_b(1-4N_b^2+6\Delta_b^2-6N_b\Delta_b)}{Z_b^2R_q^3}+\ldots\right\}. \qquad (191)\end{aligned}$$

From (169), the value of p at R_q, needed to evaluate δn_η, is

$$p|_{R_q} = R_q(Z_a - Z_b)/2(K_a - K_b). \qquad (192)$$

In the homonuclear limit, δW of (191) reduces to

$$\delta W = W_g - W_u = (-1)^m 2\mathrm{e}^{-(R/N+N)}(2R/N)^{N-\Delta}(N^3K!\,(K+m)!)^{-1}$$
$$\times\left\{1+\frac{N}{4R}(3N^2+8N\Delta-3\Delta^2-1+m^2)+\frac{N^2}{32R^2}((3N^2+8N\Delta-3\Delta^2-1+m^2)^2\right.$$
$$-48N^2-48N\Delta-28N^3-52N^2\Delta-84N\Delta^2-28N+4Nm^2+20\Delta^3$$
$$\left.+20\Delta-12\Delta m^2)+\ldots\right\}, \tag{193}$$

where I have used (126) to eliminate p. Aside from the factor of $(-1)^m$ which they omitted, this is equivalent to the H_2^+ results of Komarov & Slavyanov (1967) and Damburg & Propin (1968) (who give one higher order).

To facilitate comparison of (191) with the heteronuclear result (154) of Komarov & Slavyanov, we re-write (154) as

$$\delta W = 2|\delta n_\eta|(Z_a-Z_b)^2/(K_a-K_b)^3. \tag{194}$$

To get this result, they obviously differentiated (152) for W instead of (171). This is inconsistent, because in the homonuclear case they differentiated (171), as I have done in both cases. Also, since $K_a-K_b=\chi-\chi'=D$ is independent of δn_η, $\partial(K_a-K_b)/\partial\delta n_\eta=0$ instead of 2 as they have used. Ponomarev noted that his expression for δW, (153), does reduce to the lead term of the homonuclear result. However, the lead term of my result, (191), is not equivalent to (153) except in the homonuclear limit. I have not investigated this discrepancy any further.

For the BH^{5+} quasi-crossing, the exact splitting at $R_q=12.92$ is 4.4×10^{-3} a.u., and (191) gives $\delta W=5.1\times10^{-3}$ a.u. For OH^{8+}, the exact splitting at $R_q=16.71$ is 2.1×10^{-3}, (191) gives 2.8×10^{-3}. Formula (191) predicts $\delta W=4.1\times10^{-12}$ for the quasi-crossing at $R_q=44.31$. Using double precision arithmetic (carrying about 15 decimal digits), I can usually calculate W accurate to 12 digits with my computer program, but I am unable to evaluate accurately this particular splitting because the roots are too close together. I can only state that the exact splitting is *ca.* 10^{-12} at $R=44.316895119$. Such precision in R is required because the potential curves are intersecting sharply, so a slight change in R makes an order of magnitude change in the splitting. For instance, at $R=44.316890$, the exact energy splitting is 2.5×10^{-8}. The accuracy of the homonuclear splitting formula has been tested by Damburg & Propin against some of the exact H_2^+ energies later tabulated by Madsen & Peek (1971), with excellent agreement.

Even three orders in expansion (187) for δn_η is insufficient in many cases. For the OH^{8+} splitting at $R=16.71$, the successive terms in the $1/p$ expansion are $(1-21/2p+138/(2p)^2+\ldots)$ $=(1-0.898+0.252+\ldots)\simeq0.354$. The sum is converging very slowly, and there is thus considerable uncertainty in our result. Using the e_k transformation (Shanks 1955; Wynn 1956) to accelerate the convergence gives the estimate 0.299, which in turn gives $\delta W=2.3\times10^{-3}$, improving the agreement with the exact splitting. We really need several more orders in the $1/p$ expansion in order to extrapolate with some degree of confidence. The e_k transformation can also be used to accelerate the convergence of the $1/R$ series for W. From the work of Dalgarno & Lewis (1956), it may be most accurate to 'sum' the terms of each order in (Z_b/Z_a) separately.

Keeping just the lead terms, (178) gives

$$Y_-(\eta)\simeq(1-\eta^2)^{-\frac{1}{2}}m!\,(-1)^{K_a}\{(2p(1+n))^{\chi_0}(2/(1-\eta))^{\chi_0-D}\mathrm{e}^{-p(1+\eta)}/(K_a+m)!$$
$$-\delta n_\eta K_a!(\tfrac{1}{2}(1-\eta))^{\chi_0-D}(2p(1+\eta))^{-\chi_0}\mathrm{e}^{p(1+\eta)}\} \tag{195}$$

for a centre a s.a. state, where $\chi_0 = K_a + \frac{1}{2}(m+1)$. This expression for the dominant term in $Y_-(\eta)$ is valid *inside* the barrier separating the two wells. When $\delta n_\eta \sim \exp(-4p)$, as it is away from a quasi-crossing, the second term in (195) is exponentially smaller than the first term, and completely negligible. At a quasi-crossing, using (187) gives

$$Y_-(\eta) \simeq (1-\eta^2)^{-\frac{1}{2}} m!(-1)^{K_a}\{(2p(1+\eta))^{\chi_0}(2/(1-\eta))^{\chi_0-D} e^{-p(1+\eta)}/(K_a+m)! \mp K_a!\, 2^{\chi_0}(4p)^{\chi_0'}(\tfrac{1}{2}(1-\eta))^{\chi_0-D}(1+\eta)^{-\chi_0} e^{p(\eta-1)}(K_a!(K_a+m)!\,K_b!(K_b+m)!)^{-\frac{1}{2}}\}. \quad (196)$$

The two terms are now of comparable magnitude near $\eta = 0$. Moving towards $\eta = \pm 1$, the first term is decreasing exponentially and the second increasing exponentially, so that the first term is the asymptotic limit of Ψ^a, the second, of Ψ^b. The wavefunction is increasing exponentially as we penetrate through the barrier into either well, and the electron is thus shared by both wells. Note that when δn_η is positive (upper sign in (196)), the wavefunction has a node inside the barrier, just as $Y(\eta)$ odd has a node at $\eta = 0$ in the homonuclear case.

Assume that $Z_a > Z_b$ and let two states be specified by the u.a. quantum numbers nlm and $n'l'm'$. Let us gather together the conditions for a quasi-crossing of their potential curves as R is decreased from an initial value larger than any possible R_q. If one or both of these states quasi-crosses with one or more different states as R is decreased, we substitute the quantum numbers of the state(s) of the most recent quasi-crossing(s) to continue the investigation at smaller R values. Let us assume that nlm and $n'l'm'$ are still the appropriate quantum numbers. We must have: (1) $n-l = n'-l'$ and $m = m'$ so that n_ξ and n_ϕ are the same for both states; (2) if nlm correlates with a centre a s.a. state, $N_a K_a m$, then $n'l'm'$ must correlate with a centre b s.a. state, $N_b K_b m$, and vice versa; (3) since $Z_a > Z_b$, we must have $Z_a/N_a < Z_b/N_b$ to have a possible intersection of the $1/R$ curves; (4) with R_q given by (173) and $W(R_q)$ by (152), we must have $W(R_q) < U_{\max}(R_q)$, otherwise the $1/R$ expansions are invalid.

For example, consider $Z_b = 1$. The state with $n'l'm' = Z_a, Z_a-1, 0$ correlates with the s.a. limit hydrogen atom ground state, $N_b K_b m = 100$. The first state with which it could possibly quasi-cross is $nlm = Z_a-1, Z_a-2, 0$, which gives $N_a K_a m = Z_a-1, Z_a-2, 0$. The energy at R_q is then $-(Z_a-1)^2/2(Z_a-2)^2$, so we must restrict $Z_a > 2$. With $Z_a = 3$ and 4, we find $R_q < R_x$, so these crossings are meaningless. The first quasi-crossing occurs with $Z_a = 5$.

Neither Ponomarev nor Komarov & Slavyanov recognized that the $1/R$ series energy should be (171) at R_q. Instead, both used equations of the form

$$-(Z_a-Z_b)^2/2(K_a-K_b)^2 = -Z_a^2/2N_a^2 - Z_b/R + \ldots = -Z_b^2/2N_b^2 - Z_a/R + \ldots \quad (197)$$

to find R_q. The rates of convergence of the two series are quite different, so Ponomarev, who only had these series through $O(1/R^2)$, noted considerable fluctuation in his value of R_q depending upon which of the equalities in (197) was used. Ponomarev has given a lucid discussion of quasi-crossings. By truncating $W(R)$ at $O(1/R)$, he was able to obtain an analytical expression for the number of quasi-crossings. This truncation limits the accuracy of his results, and a case which is close one way or the other should be tested directly as I have indicated above, with the inclusion of higher order terms.

It has been suggested in the work of Gershtein & Krivchenkov (1961) and Ponomarev & Puzynina (1967) that these results on intersections of potential curves of the same geometrical symmetries and on quasi-crossings may be used in discussing processes such as charge exchange involving the hydrogen mesic atom and a nucleus. All of our results, including the very existence of potential curves, are based on the assumption that we can ignore the nuclear motion. This is

not too bad an approximation for the systems $Z_a e^- Z_b$, where the nuclear masses are several thousand times larger than the electron's mass. It is a very poor approximation for $Z_a \mu^- Z_b$, where the nuclear masses are only about 10 times larger than that of the μ^- meson, so these results should be used in such cases only with much scepticism.

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Appendix 1. Divergence of the continued fraction for $Y(\eta)$

The expansion

$$Y(\eta) = (1-\eta^2)^{\frac{1}{2}m} \exp(-p(1+\eta)) \sum_{j=0}^{\infty} h_j L_j^m(2p(1+\eta)) \tag{A 1}$$

has been suggested by Buckingham (1961) and Ponomarev & Puzynina (1968), and is a special case of (87) with $\delta n_\eta = 0$. The continued fractions resulting from these expansions do *not* converge. Either the expansions (87) and (A 1) are themselves divergent, or else the ratios h_{j+1}/h_j are not given by the continued fractions analogous to (90).

If we replace α_i, β_i and γ_i in (85) by $s_i\alpha_i$, $s_i\beta_i$ and $s_i\gamma_i$, where $s_i \neq 0$, and then proceed as before, we get

$$s_i\gamma_i h_{i+1}/h_i = -\frac{s_i s_{i+1}\gamma_i\alpha_{i+1}}{s_{i+1}\beta_{i+1} -} \frac{s_{i+1}s_{i+2}\gamma_{i+1}\alpha_{i+2}}{s_{i+2}\beta_{i+2} -} \cdots. \tag{A 2}$$

This is known as an equivalence transformation, and does not affect the value of the continued fraction. Taking $s_i = 1/\beta_i$, we have a continued fraction of the form

$$\frac{\nu_i}{1-} \frac{\nu_{i+1}}{1-} \frac{\nu_{i+2}}{1-} \cdots, \tag{A 3}$$

with $\nu_i = \gamma_i\alpha_{i+1}/\beta_i\beta_{i+1}$. A necessary condition for the convergence of a continued fraction is that its 'tail' converge, so we can choose $i \gg p$ in (A 3) to investigate convergence. We find that $\nu_i = (\frac{1}{4} + p/i + \ldots)$ for both (87) and (A 1). Blanch (1964) proves that one must have $\nu_i \leqslant \frac{1}{4}$ in order for a continued fraction of the form (A 3) with $\nu_i \geqslant 0$ to converge, so the continued fractions from (87) and (A 1) both fail to converge. Their successive approximates $f_n = A_n/B_n$ form an asymptotic series, and we were not wrong in using them to get the asymptotic expansion $\tilde{C}_\eta$. For the continued fraction from the outer equation, we have $\nu_i = (\frac{1}{4} - p/i + \ldots)$, so it converges.

When we substitute (A 1) into the inner equation, we get

$$\sum_{j=0}^{\infty} \{\alpha_j h_{j-1} + \beta_j h_j + \gamma_j h_{j+1}\} L_j^m(2p(1+\eta)) = 0, \tag{A 4}$$

where α_i, β_i and γ_i are given by (86) with $S \to D$ and $p \to -p$. The functions L_j^m are linearly independent, so the only way that (A 4) can be true for the denumerably infinite set of terms in

the sum while η ranges over the non-denumerably infinite continuum of values of η in $(-1, 1)$ is to have

$$\alpha_j h_{j-1} + \beta_j h_j + \gamma_j h_{j+1} = 0. \tag{A 5}$$

If instead of (A 1), we use

$$Y(\eta) = (1-\eta^2)^{m/2} \exp(-p(1+\eta)) \sum_{j=0}^{\infty} h_j (2p(1+\eta))^j, \tag{A 6}$$

we get an equation of the form (A 4) with different coefficients and with $L_j^m(2p(1+\eta))$ replaced by $(2p(1+\eta))^j$. We can use either the above argument or a theorem on power series to get (A 5). Baber & Hassé (1935) proved that (A 6) converges. When we use the analogue of (A 1) for the outer equation, (84), we can multiply (A 4) by $\exp(-\frac{1}{2}x)\, L_i^m(x)$, where $x = 2p(\xi - 1)$, and integrate from $x = 0$ to ∞ and use the orthogonality of the associated Laguerre polynomials to get (A 5). We cannot do this for (A 1), because $2p(1+\eta)$ ranges only between 0 and $4p$, and instead of giving zero when $i \neq j$, we would get integrals $\sim \exp(-4p)$. Even if the first argument for going from (A 4) to (A 5) is somehow wrong and we have to use the above approach, we can completely ignore exponentially small terms when finding the $1/p$ expansion, so our previous result for $\tilde{C}_\eta$ remains valid. It is not clear whether the continued fractions from (87) and (A 1) diverge because these expansions themselves diverge, or because we have somehow erred in going from (A 4) to (A 5).

Appendix 2. Asymptotic expansion by perturbation theory

A recurrence relation such as (85) is equivalent to the infinite matrix equation

$$\boldsymbol{M}\boldsymbol{g} = \boldsymbol{0}, \tag{A 7}$$

where $\boldsymbol{g}$ is an infinite column vector with elements $g_0, g_1, g_2, \ldots$, $\boldsymbol{0}$ is the infinite zero column vector, and $\boldsymbol{M}$ is an infinite matrix with elements

$$M_{i,j} = \alpha_i \delta_{i,j-1} + \beta_i \delta_{i,j} + \gamma_i \delta_{i,j+1}, \tag{A 8}$$

where $\delta_{i,j}$ is the Kronecker delta. In order to have a non-trivial solution for the g_i, the determinant of $\boldsymbol{M}$ must be zero. Defining the truncated determinants

$$\det_1 = \beta_0, \quad \det_2 = \begin{vmatrix} \beta_0 & \gamma_0 \\ \alpha_1 & \beta_1 \end{vmatrix}, \quad \det_3 = \begin{vmatrix} \beta_0 & \gamma_0 & 0 \\ \alpha_1 & \beta_1 & \gamma_1 \\ 0 & \alpha_2 & \beta_2 \end{vmatrix}, \ldots, \tag{A 9}$$

the value of the infinite determinant is $\lim_{i\to\infty} \det_i$. By expanding $\det_i$ by cofactors of its ith row or column, one finds

$$\det_i = \beta_{i-1} \det_{i-1} - \gamma_{i-2}\alpha_{i-1} \det_{i-2}. \tag{A 10}$$

This is the same recurrence relation as (97) for the numerators and denominators of the continued fractions; one can show that $\det_i$ are equivalent to the numerators.

Consider the solution of

$$(H^0 + \lambda V - E_i)\, \Psi_i = 0 \tag{A 11}$$

by perturbation theory. We assume that we can expand

$$\left.\begin{aligned} \Psi_i &= \Psi_i^0 + \lambda \Psi_i^1 + \lambda^2 \Psi_i^2 + \ldots, \\ E_i &= E_i^0 + \lambda E_i^1 + \lambda^2 E_i^2 + \ldots, \end{aligned}\right\} \tag{A 12}$$

and solve the resulting equations by expanding $\Psi_i^1, \Psi_i^2, \ldots$, in terms of the complete set of zero-order wavefunctions. One finds (Hirschfelder, Epstein & Byers-Brown 1964)

$$E_i^1 = V_{ii}; \quad E_i^2 = \sum_j{}' \frac{V_{ij}V_{ji}}{E_i^0 - E_j^0}; \quad E_i^3 = \sum_j{}' \sum_k{}' \frac{V_{ij}V'_{jk}V_{ki}}{(E_i^0 - E_j^0)(E_i^0 - E_k^0)}; \quad \text{etc.}, \tag{A 13}$$

where $V_{jk} = \langle \Psi_j^0 | V | \Psi_k^0 \rangle$ and $V'_{jk} = V_{jk} - V_{ii}\delta_{j,k}$. The prime on Σ deletes i from the infinite summation-integration over all states.

On the other hand, suppose that we directly expand the total wavefunction Ψ_i in (A 11) in the basis set of zero-order functions. In order to have a non-trivial solution, the determinant of elimination must vanish,

$$\begin{vmatrix} E_0^0 + \lambda V_{00} - E_i & \lambda V_{01} & \lambda V_{02} & \\ \lambda V_{10} & E_1^0 + \lambda V_{11} - E_i & \lambda V_{12} & \\ \lambda V_{20} & \lambda V_{21} & E_2^0 + \lambda V_{22} - E_i & \\ & & & \ddots \end{vmatrix} = 0. \tag{A 14}$$

Solving this determinant for E_i, we express the result as a power series in λ; it obviously must be equivalent to the perturbation expansion (A 12) of E_i.

Dividing all of the elements of M by p and using (104) to (109), we see that det $(M) = 0$ is a special tridiagonal case of (A 14) if we identify $1/p$ with λ and C/p with E_i. We can thus use the perturbation energy formulae (A 13) to get the $1/p$ expansion of C. We have $E_i^0 - E_{i+k}^0 = 4k$ in the denominators. Only $j = i \pm 1$ contribute to the sum over states in E_i^2, because $V_{ij} = 0$ except for $j = i$ and $i \pm 1$, and thus

$$E_i^2 = \tfrac{1}{4}(V_{i,i+1}V_{i+1,i} - V_{i,i-1}V_{i-1,i}). \tag{A 15}$$

In the third-order energy sums, the only non-vanishing terms are $j = k = i \pm 1$, and through third-order we find (115), derived earlier via the continued fraction.

I actually obtained $\tilde{C}_\xi$ in (119) by evaluating the perturbation energies through sixth-order. I later discovered the equivalence of this approach to the continued fraction method described in the body of the paper. Both methods have their merits. I believe that it would be easier to find higher order terms via the continued fraction. Also, the derivation of the $1/p$ expansion of $\tilde{C}_\xi$ from the convergent successive approximations to the continued fraction clearly showed that the $1/p$ series is asymptotic. With the perturbation expansion of the determinant, it is obvious that if the matrix elements away from the tridiagonal were not identically zero but were exponentially small in p, they could be ignored in getting the $1/p$ expansion.

Appendix 3. Exact analytical solutions

Demkov (1968) has shown from fundamental considerations that $X(\xi)$ and $Y(\eta)$ can have exact elementary solutions when S and D are integers. This also follows directly from our series solutions. Let $Z_a > Z_b$, so $D > 0$. With expansion (A 1), we have $\alpha_i = i(i+m) - iD$ in the three-term recurrence relation; with (A 6), $\alpha_i = 2(i+m-D)$. When $D = i+m$, $\alpha_i = 0$, and both of these expansions terminate exactly after i terms. The centre b expansions, with $D \to -D$ in the recurrence relations, cannot terminate.

If (A 1) and (A 6) both terminate, we can regroup terms to change one expansion into the other. With D an integer, we find also that their truncated determinants give identical equations for C. This seems to indicate that we have not ignored terms $\sim \exp(-4p)$ in getting the three-term recurrence relation from (A 1), and that (A 1) is an asymptotic expansion unless it accidentally

truncates. With $m = 0$ and $D = 2$, the 2×2 determinants from (A 1) and (A 6) both give $C^2 - 2C - 4p^2 = 0$, so

$$\begin{aligned} \tilde{C}_\eta &= 1 \pm 2p(1 + 1/4p^2)^{\frac{1}{2}} \\ &= \pm 2p + 1 \pm 4p \mp 1/64p^3 \pm 1/512p^5 + \ldots . \end{aligned} \tag{A 16}$$

This checks with our general expansion for $\tilde{C}_\eta$ using $D = 2$ and $K_a = 0$ or 1.

Each of the potential curves for BH^{5+} in figure 2 has $D = 3$ at their intersection with the line $W = \frac{8}{9}$. The series expansion for $Y(\eta)$ thus truncates after three terms and is *exact* at $R \simeq 13.03$. We see from this, and could also find directly from (186), that $\delta n_\eta = 0$ for the 4fσ state at this point. Although $\tilde{C}_\eta$ is exact, $\tilde{C}_\xi$ is still asymptotic, so the expansion of W in powers of $1/R$ remains an asymptotic series at this point. Calculating terms higher than sixth-order would probably improve the agreement between the $1/R$ and exact potential curves from a difference of about 1.5×10^{-3} hartrees in figure 5 down to about 1.0×10^{-3}. With $\delta n_\eta = 0$ at $R = 13.03$, this error remains when we make the Taylor series expansion (189) about $\delta n_\eta = 0$. Note that δn_η for the 5gσ state is equal to that for the 4fσ only at $R = R_q$, and in general the errors in the two $1/R$ curves are not the same both before and after the $O(\delta n_\eta)$ corrections. We thus can expect to have an uncertainty of about 10^{-3} hartree in our estimate of δW at R_q in this particular case.

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