PHYSICAL REVIEW A VOLUME 31, NUMBER 4 APRIL 1985

Long-range couplings in the adiabatic hyperspherical basis

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(Received 7 May 1984)

The infinite set of coupled equations in the adiabatic hyperspherical representation of two-electron correlated states is solved in the asymptotic region. The solution reveals that the longest-range couplings represent a partial transformation to independent-electron coordinates. Simple corrections to the phase shifts of H^- are obtained. Adiabatic and corrected phase shifts in the monopole approximation are compared with the Hartree-Fock phase shifts. Good agreement is obtained. The correction is applied to previously reported adiabatic phase shifts.

I. INTRODUCTION

Electron correlations play a role, to a greater or lesser degree, in the structure of all multielectron atoms, molecules, and solids. In the early 1960s it was recognized that most multiply excited atomic states, i.e., states in which two or more electrons share excitation energy, were so highly correlated that an independent-particle model represented a poor zeroth-order approximation.[1] In the search for a more comprehensive description of such states, several approaches have proved valuable.[1-8] The adiabatic hyperspherical approximation is notable in defining reaction channels characterized by a potential function[4,5,9] $U_{\mu\mu}(R)$. For two-electron atoms and ions, which are the systems considered in this paper, R is given in terms of the radial coordinates r_1 and r_2 of the electrons by $R=(r_1^2+r_2^2)^{1/2}$. Additionally, five hyperangles are needed to specify the electron positions in configuration space. Many choices for these angles exist;[10-12] we use the hyperangle $\alpha=\arctan(r_2/r_1)$ and the polar coordinates $\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2$ of the two electrons. The set of five angles is denoted collectively by Ω. Atomic units are used throughout.

The properties of correlated states are determined in the adiabatic approximation by a set of adiabatic functions $\phi_\mu(R;\Omega)$ obtained by solving the Schrödinger equation at fixed R and associated potentials $U_{\mu\mu}(R)$. The one-channel radial equations in R are then solved to obtain phase shifts, bound-state energies, and quantum defects. This approach has proved valuable in classifying and interpreting the energies, widths, oscillator strengths, and wave functions of highly correlated states.[4,9,13] Qualitative insights into electron excitation[13] have been achieved. The approximation also provides a point of departure for interpreting electron correlations in many-electron atoms.[14]

While the main successes of the adiabatic hyperspherical approximation have been qualitative, it also provides a well-defined basis for quantitative calculations. The approximation is remarkably accurate when the two electrons are highly correlated and share excitation energy equally. For example, the ground-state energy of H^- is found within 0.01 eV, of the best accepted value using only one hyperspherical channel.[9] When the electron motion becomes less correlated, as for states with electrons in different shells,[4] or with significantly differing excitation energies, the approximation becomes less accurate. Indeed, for continuum states of H^- 5 eV above the ground state, a few-channel (even a one-channel or Hartree-Fock[15]) close-coupling description is quantitatively more accurate. Adiabatic hyperspherical states thus describe correlations accurately, but only imperfectly represent simple independent-particle motion. Since correlated states and independent-particle states coexist, the failure of the adiabatic representation to accurately describe the independent-particle motion is a serious drawback. A particularly notable manifestation of this problem is seen in the H^- ^1S phase shifts calculated by Lin.[9,16] They compare favorably with the best available results at electron energies of the order of 0.01 a.u., but are considerably in error at 0.25 a.u.

In principle, the adiabatic approximation can be improved by incorporating more coupled channels. Since the differential equations are purely local and there are no explicit, nonlocal exchange terms, such calculations are tractable.[17] Because, as will be shown, the expansion converges slowly at large R, this does not really solve the problem. A more direct approach is to match, approximately, the close-coupling solutions to the adiabatic solutions at some intermediate R. Calculations by Christensen-Dalsgaard[18] using this method show definitely that the difference between adiabatic and Hartree-Fock phase shifts is due to poor representation of the motion at large R in the adiabatic approximation.

In this paper we seek a more detailed explanation of the effects discovered by Christensen-Dalsgaard. To this end we obtain a closed-form solution valid to order $1/R^2$ for the infinite set of coupled equations at large R. This solution implies that the coordinate R approaches the single-particle coordinate r_1 as $r_1\rightarrow\infty$, with r_2 fixed, too slowly to give an accurate representation of the motion at large R for all except the lowest energies. A simple correction to the phase shift is derived from the asymptotic solution and is applied to the model of Ref. 18. Some implications of the results are discussed.

II. ASYMPTOTIC SOLUTIONS

A. Review of the hyperspherical adiabatic expansion

The coupled differential equations in the hyperspherical representation have been given in several references.[4,5,11,13,19] The notation of Lin[5] is used throughout.

The Schrödinger equation for two electrons in a He-like ion is

$$\left[\nabla_1^2+\nabla_2^2+\frac{2Z}{r_1}+\frac{2Z}{r_2}-\frac{2}{r_{12}}+2E\right]\psi=0 . \tag{1}$$

In the hyperspherical coordinates defined in the Introduction, Eq. (1) becomes

$$\left[\frac{d^2}{dR^2}-\frac{\Lambda^2+\frac{15}{4}-RC}{R^2}+2E\right]R^{5/2}\psi=0 , \tag{2}$$

where the generalized angular momentum operator Λ^2 is defined by

$$\begin{aligned}\Lambda^2=&-\frac{1}{\sin^2\alpha\cos^2\alpha}\frac{d}{d\alpha}\sin^2\alpha\cos^2\alpha\frac{d}{d\alpha}\\&+\frac{l_1^2}{\cos^2\alpha}+\frac{l_2^2}{\sin^2\alpha} ,\end{aligned} \tag{3}$$

and the function $C(\alpha,\theta_{12})$ is given by

$$C=2Z/\cos\alpha+2Z/\sin\alpha-2/(1-\sin^2\alpha\cos\theta_{12})^{1/2} . \tag{4}$$

Because $C(\alpha,\theta_{12})$ is divided by R rather than R^2, Eq. (2) is not separable in the hyperspherical coordinates. The essential idea of Ref. 4 is that, because the linear variation of the potential term in $\Lambda^2-RC(\alpha,\theta_{12})$ is in some sense slow or adiabatic, Eq. (2) is approximately separable. Thus we define a complete orthonormal set of eigenfunctions $\phi_\mu(R;\Omega)$ of the operator $\Lambda^2+\frac{15}{4}-RC(\alpha,\theta_{12})$ with eigenvalues $R^2U_{\mu\mu}(R)$. The functions are solutions of the equation

$$\begin{aligned}(-\Lambda^2-\tfrac{15}{4}&+RC)(\sin\alpha\cos\alpha)^{-1}\phi_\mu(R;\Omega)\\&=-R^2U_{\mu\mu}(R)(\sin\alpha\cos\alpha)^{-1}\phi_\mu(R;\Omega) .\end{aligned} \tag{5}$$

The factors $(\sin\alpha\cos\alpha)^{-1}$ and $-\frac{15}{4}$ are introduced so that the functions $\phi_\mu(R;\Omega)$ agree with those defined in Ref. 4.

The wave function ψ is expanded as

$$R^{5/2}\psi(R,\Omega)=\sum_\nu F_\nu(R)(\sin\alpha\cos\alpha)^{-1}\phi_\nu(R;\Omega) , \tag{6}$$

which leads to the coupled equations for the expansion coefficients $F_\mu(R)$:

$$\begin{aligned}\left[\frac{d^2}{dR^2}-U_{\mu\mu}(R)+\frac{0.25}{R^2}+W_{\mu\mu}(R)+2E\right]&F_\mu(R)\\&=-\sum_{\nu\,(\neq\mu)}W_{\mu\nu}F_\nu(R) ,\end{aligned} \tag{7}$$

where

$$\begin{aligned}W_{\mu\nu}=2&\left[\phi_\mu(R;\Omega),\frac{d}{dR}\phi_\nu(R;\Omega)\right]\frac{d}{dR}\\&+\left[\phi_\mu(R,\Omega),\frac{d^2}{dR^2}\phi_\nu(R;\Omega)\right] .\end{aligned} \tag{8}$$

The inner product in Eq. (8) represents integration with respect to the five angular coordinates using a volume element $d\alpha\, d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2$.

B. Asymptotic equations

We are interested in the solutions to the radial equations Eq. (7) as $R\rightarrow\infty$. To this end we need the large-R limit of the adiabatic functions.[4] From Ref. 4 one has

$$\phi_\mu(R;\Omega)\rightarrow N\sum_{l_1l_2}P_\mu(R\sin\alpha)\mathscr{Y}^M_{l_{1\mu}l_{2\mu}L}(r_1,r_2)A_{l_1l_2,\mu} , \tag{9}$$

where $P_\mu(r)$ is a hydrogenic radial function, $\mathscr{Y}^M_{l_1l_2L}$ is defined by

$$\begin{aligned}\mathscr{Y}^M_{l_1l_2L}&(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\\&=\sum_{m_1,m_2}(LM\mid l_1m_1l_2m_2)Y_{l_1}^{m_1}(\hat{\mathbf{r}}_1)Y_{l_2}^{m_2}(\hat{\mathbf{r}}_2) ,\end{aligned} \tag{10}$$

and N is a normalization constant depending upon R. The coefficients A are determined by diagonalizing the dipole potential[4,6] in the space of degenerate n levels. Since our approximate solutions at large R include the complete set of adiabatic functions, we can use a representation in which

$$\phi_\mu(R;\Omega)\rightarrow P_\mu(r_2)\mathscr{Y}^M_{l_{1\mu}l_{2\mu}L}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2) . \tag{11}$$

Use of the simpler functions of Eq. (11) means that our complete basis set is not strictly the adiabatic set, but is related to it by a unitary transformation. Since the unitary transformation is made only at large R and mixes only degenerate functions, it can be made before or after solving the asymptotic equations. Because the solution proceeds more simply in the representation Eq. (11), it is the one used here. To compensate for the change of representation we must add to $W_{\mu\nu}(R)$ a term $d_{\mu\nu}/R^2$ representing the dipole coupling between degenerate levels.

Our objective is to solve the set of coupled equations as an asymptotic series in inverse power of R. To that end we need the asymptotic form of the coupling matrix elements. Substituting the asymptotic solutions from Eq. (11) into the expression for $W_{\mu\nu}$ and integrating over the coordinates $\hat{r}_1,\hat{r}_2$ gives

$$\begin{aligned}\left[\phi_\mu(R;\Omega),\frac{d}{dR}f_\nu(R;\Omega)\right]&\\=\int_0^{\pi/4}N_\mu P_\mu(R\sin\alpha)&\frac{d}{dR}[N_\nu P_\nu(R\sin\alpha)]d\alpha ,\end{aligned} \tag{12}$$

where

$$N_\mu^{-2}=\int_0^{\pi/4}P_\mu^2(R\sin\alpha)d\alpha . \tag{13}$$

The integral over α in Eqs. (12) and (13) extends only to $\pi/4$ since, as shown in Ref. 4, use of symmetry with respect to interchange of like particles reduces the region of definition of the problem to the region $0 \leqq \alpha \leqq \pi/4$. Indeed, the asumptotic form of Eq. (9) implies that $\alpha < \pi/4$.

Setting $R\sin\alpha = r$, expanding the differential volume element through first order in $1/R$, replacing the upper limit of integration $R/\sqrt{2}$ by infinity, and using the orthogonality of the function $P_\mu(r)$, we have

$$N_\mu = \sqrt{R} \ , \tag{14}$$

and

$$\left[\phi_\mu(R;\Omega), \frac{d}{dR}\phi_\nu(R;\Omega)\right] \approx N_\mu \frac{dN_\nu}{dR} \int_0^{\pi/4} P_\mu(R\sin\alpha) P_\nu(R\sin\alpha) d\alpha + N_\mu N_\nu \int_0^{\pi/4} P_\mu(R\sin\alpha)\sin\alpha P'_\nu(R\sin\alpha) d\alpha$$

$$\approx R^{-1} \int_0^\infty P_\mu(r) r P'_\nu(r) dr = (P_\mu, rP'_\nu)/R \equiv A_{\mu\nu}/R \ . \tag{15}$$

Similarly, for the matrix element of the second-derivative operator we have

$$\left[\phi_\mu(R;\Omega), \frac{d^2}{dR^2}\phi_\nu(R;\Omega)\right] \approx \int_0^{\pi/4} N_\mu P_\mu(R\sin\alpha) \frac{d^2}{dR^2} N_\nu P_\nu(R\sin\alpha) d\alpha$$

$$\approx \frac{2N_\mu}{R}\frac{dN_\nu}{dR}(P_\mu, rP'_\nu) + \frac{N_\mu N_\nu}{R^2}(P_\mu, r^2 P''_\nu)$$

$$= [-2(P_\mu, rP'_\nu) + (P_\mu, r^2 P_{\nu''})]/R^2 \equiv b_{\mu\nu}/R^2 \ . \tag{16}$$

To order $1/R^2$, Eq. (7) becomes[3]

$$\left[\frac{d^2}{dR^2} - \frac{l_{1\mu}(l_{1\mu}+1)}{R^2} + \frac{2(Z-1)}{R} + k_\mu^2\right] F_\mu = -\sum_\nu 2\frac{a_{\mu\nu}}{R}\frac{dF_\nu}{dR} + \frac{b_{\mu\nu}+d_{\mu\nu}}{R^2} F_\nu \ , \tag{17}$$

where $d_{\mu\nu}$ vanishes if $k_\mu^2 \neq k_\nu^2$.

We seek a solution to these equations valid through order $1/R$. Both the diagonal potential terms and the coupling terms contribute to this order. While it is not difficult to solve the equations for any value of L and Z, the resulting solutions contain terms of order $1/R$ which originate from both the diagonal potential terms and the nondiagonal coupling terms. Since the contributions from the diagonal terms are already incorporated in the one-channel adiabatic approximation, and since the objective is to identify the effect of the coupling terms to this order, we consider the special case with $\ell_{1\mu} = 0$ and $Z - 1 = 0$, i.e., s waves of H$^-$. In this case the diagonal angular momentum and potential terms vanish in the asymptotic limit. The general case is easily inferred from this special case, although it can also be obtained directly.

With these simplifications the coupled equations are

$$\left[\frac{d^2}{dR^2} + k_\mu^2\right] F_\mu = -\sum_\nu \left[2\frac{a_{\mu\nu}}{R}\frac{dF_\nu}{dR} + \frac{b_{\mu\nu}+d_{\mu\nu}}{R^2} F_\nu\right] . \tag{18}$$

The boundary conditions on the solutions require standing waves in one channel, which is taken to be the channel μ, and no waves in any other channels as $R \to \infty$.

At finite R there will be waves in all channels, but their amplitudes must vanish as $1/R$ or faster. Acceptable solutions to order $1/R$ then have the form

$$F_\mu(R) = \sin(k_\mu R + \delta) + \cos(k_\mu R + \delta) B_\mu/R \ , \tag{19}$$

and

$$F_\nu(R) = \cos(k_\mu R + \delta) A_\nu/R \ , \quad \nu \neq \mu \ . \tag{20}$$

Equations (19) and (20) represent the first nonvanishing terms of an asymptotic expansion to $F_\mu(R)$.

As is usual for expansions at large R there are two independent solutions usually denoted by $\mathscr{F}$ and $\mathscr{G}$. Such solutions are obtained from our Eqs. (19) and (20) by setting $\delta = 0$ to obtain the "$\mathscr{F}$" or sine-like solution and $\delta = \pi/2$ to obtain the "$\mathscr{G}$" or cosine-like solution. The pair of solutions is then added to obtain the general solutions at large distances $F \approx \mathscr{F} + \mathscr{G}K$, where K is determined by matching the logarithmic derivative of F to a solution in the inner region. In the general case, $\mathscr{F}$, $\mathscr{G}$, and K are matrices. It is not necessary to employ the matrix notation if we seek solutions valid only through order $1/R$. Solutions employing the matrix notation are discussed in the Appendix. Because $\ell_{1\mu} = 0$, the amplitude of the sine wave contains no $1/R$ terms. Equation (19) makes explicit use of this information.

Substituting $F_\nu(R)$ from Eqs. (19) and (20) into Eq. (18) and equating to zero coefficients of like powers of R gives the results

$$A_\nu = -2a_{\nu\mu}k_\mu/(k_\nu^2 - k_\mu^2) = -a_{\nu\mu}k_\mu/(E_\mu - E_\nu) \ , \tag{21}$$

where E_μ is an eigenenergy of the hydrogen atom. The constant B_μ is similarly found to be

$$B_\mu = \sum_\nu a_{\mu\nu} A_\nu = -k_\mu \sum_\nu a_{\mu\nu} a_{\nu\mu}/(E_\mu - E_\nu) \ . \tag{22}$$

The total six-variable wave function of Eq. (2) at large R becomes

$$\sin\alpha\cos\alpha\, R^{5/2}\psi(R,\Omega)=\left\{P_\mu(r_2)[\sin(k_\mu R+\delta)+(B_\mu/R)\cos(k_\mu R+\delta)] - \sum_{\nu\neq\mu} k_\mu P_\nu(r_2)[a_{\nu\mu}/(E_\mu-E_\nu)]\cos(k_\mu R+\delta)\right\}\mathcal{Y}^M_{l_{1\mu}l_{2\mu}L}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\ . \tag{23}$$

The sum over ν on the right-hand side of Eq. (23) has the form of a first-order perturbed wave function. Such sums represent the solution of inhomogeneous differential equations and are frequently amenable to direct integration.[20] To that end consider the radial equation for P_μ:

$$P''_\mu(r)+[-l_{2\mu}(l_{2\mu}+1)/r^2+2Z/r+2E_\mu]P_\mu(r)=0\ . \tag{24}$$

It follows from Eq. (24) that $f(r)=r^2P_\mu(r)$ is a solution of the inhomogeneous equation

$$f''(r)+[-l_{2\mu}(l_{2\mu}+1)/r^2+2Z/r+2E_\mu]f(r) =4rP'_\mu(r)+2P_\mu(r)\ . \tag{25}$$

Because the right-hand side of Eq. (25) is orthogonal to $P_\mu(r)$ the equation has a solution given by

$$f(r)=2\sum_\nu P_\nu(r)(P_\nu, rP'_\nu)/(E_\mu-E_\nu)+C_\mu P_\mu(r)\ , \tag{26}$$

where C_μ is a constant chosen so that $f(r)=r^2P_\mu(r)$:

$$C_\mu=(P_\mu, r^2P_\mu)\ . \tag{27}$$

Recalling Eq. (26) we have for the sum over ν in Eq. (23) the result

$$\sum_\nu P_\nu(r_2)a_{\nu\mu}/(E_\mu-E_\nu)=\sum_\nu P_\nu(r_2)(P_\nu, rP'_\mu)/(E_\mu-E_\nu) =\tfrac{1}{2}(r_2^2-C_\mu)P_\mu(r_2)\ . \tag{28}$$

Equation (28) gives a closed-form expression for the sum in Eq. (23). The asymptotic form of $\psi(R,\Omega)$ is then

$$\sin\alpha\cos\alpha\, R^{5/2}\psi(R,\Omega)=P_\mu(r_2)\{\sin(k_\mu R+\delta)+\cos(k_\mu R+\delta)\times[k_\mu(-r_2^2+C_\mu)/2+B_\mu]/R\}\mathcal{Y}^M_{l_{1\mu}l_{2\mu}L}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\ . \tag{29}$$

It remains to evaluate B_μ of Eq. (22). Forming the inner product of Eq. (28) with $rP'_\mu(r)$ and using the definition of $a_{\mu\nu}$ and the relation $a_{\mu\nu}=-a_{\nu\mu}$ gives

$$B_\mu=-k_\mu\sum_{\nu\neq\mu} a_{\mu\nu}a_{\nu\mu}/(E_\mu-E_\nu) =k_\mu(rP'_\mu,[r^2-C_\mu]P_\mu)/2\ . \tag{30}$$

The right-hand side of Eq. (30) is readily evaluated by integration by parts to obtain the desired result

$$B_\mu=-k_\mu C_\mu/2\ . \tag{31}$$

Substituting Eq. (31) into Eq. (29) gives the complete asymptotic form (valid through order $1/R$)

$$R^{5/2}\psi(R,\Omega)=P_\mu(r_2)[\sin(k_\mu R+\delta) -(k_\mu r_2^2/2R)\cos(k_\mu R+\delta)] \times\mathcal{Y}^M_{l_{1\mu}l_{2\mu}L}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\ . \tag{32}$$

To interpret this result, note that $k_\mu r_2^2/R$ is small compared with unity, and it is permissible to write

$$\sin(k_\mu R+\delta)-(k_\mu r_2^2/2R)\cos(k_\mu R+\delta) \approx\sin[k_\mu(R-r_2^2/2R)+\delta]\ . \tag{33}$$

Since r_1 is large compared with r_2 we have that

$$R-r_2^2/2R\sim r_1+O(1/r_1^3)\ . \tag{34}$$

Equations (33) and (34) are the principal results of this work. They show that including the long-range derivative couplings to order $1/R$ has the effect of modifying the argument of the sine function in the asymptotic solutions. The modified argument approaches the independent particle form as $1/r_1^3$ for large r_1. In contrast, the purely adiabatic solution involves only R, which approaches r_1 only to order $1/r_1$ as $r_1\rightarrow\infty$. Furthermore, the long-range couplings modify only $F_\mu(R)$ and not the adiabatic functions $\phi_\mu(R;\Omega)$.

III. A PHASE-SHIFT CORRECTION

The asymptotic solution of Eq. (33) demonstrates the inaccuracy of the adiabatic hyperspherical functions in the region of coordinate space where R is large. Additionally, the inaccuracy, negligible for $k_\mu=0$, becomes increasingly significant for increasing k_μ. Our derivation does not determine to what extent this inaccuracy affects the functions at small R. Accordingly, matrix elements which weight the small-R region may be accurate despite inaccuracies at large R. Phase shifts, however, depend upon the integrated effect over a broad region of R and are particularly sensitive to the long-range couplings neglected in the one-channel adiabatic approximation. Such effects are implicit in Eq. (19), which incorporates a slowly varying term B_μ/R.

The function $F_\mu(R)$ is to be matched onto a function determined in the inner region at some radius R_0. If we suppose that the logarithmic derivative of the function in the inner region is not strongly affected by the coupling to other channels, then the inner solution has the form $F_\mu(R_0)=\sin(k_\mu R_0+\delta_\mu^{(\mathrm{adb})})$ on the boundary $R=R_0$. Here $\delta_\mu^{(\mathrm{adb})}$ is the adiabatic phase shift. This is to be matched onto the solution from the outer region $F_\mu(R_0)=\sin(k_\mu R_0+\delta)+\cos(k_\mu R_0+\delta)B_\mu/R_0\approx\sin(k_\mu R_0+\delta+B_\mu/R_0)$. Matching the logarithmic derivative to order $1/R_0$ then gives

$$\delta_\mu^{(\mathrm{adb})} = \delta + B_\mu / R_0 \ , \tag{35}$$

or

$$\delta = \delta_\mu^{(\mathrm{adb})} - B_\mu / R_0 \ . \tag{36}$$

To obtain the corrected phase shift $\delta_\mu^{(c)}$ we examine $F_\mu(R)$ of Eq. (19) as $R \to \infty$. Equation (19) gives

$$\begin{aligned} F_\mu(R) &\sim \sin(k_\mu R + \delta_\mu^{(\mathrm{adb})} - B_\mu / R_0) \quad \text{as } R \to \infty \\ &\equiv \sin(k_\mu R + \delta_\mu^{(c)}) \ , \end{aligned} \tag{37}$$

so that the corrected phase shift is just given by

$$\delta_\mu^{(c)} = \delta_\mu^{(\mathrm{adb})} - B_\mu / R_0 \ . \tag{38}$$

In this joining procedure we have neglected the terms $F_\nu(R_0)\phi_\nu(R_0;\Omega)$ with $\mu \neq \nu$. These are of order $1/R_0$ and it might appear that such neglect is unwarranted, but, because these terms have $\mu \neq \nu$, they contribute to the phase shift only in second order and are thus negligible to the order that we have calculated the wave function asymptotically. While these results seem quite plausible, a rigorous proof is given in the Appendix.

Recalling Eq. (31) we have

$$\delta_\mu^{(c)} = \delta_\mu^{(\mathrm{adb})} + k_\mu C_\mu / 2R_0 \ . \tag{39}$$

According to Eq. (27) C_μ is positive definite so that the long-range couplings always serve to increase the phase shift. This is in accord with theorems[21] that including more closed coupled channels always increases the phase shift.

The phase-shift correction of Eq. (39) contains one parameter, namely the matching radius R_0. Reference 18 provides some indication of the appropriate values for R_0. There, model calculations of H^- phase shifts in which only the monopole electron-electron interaction is retained employ an R_0 equal to 6 a.u. This value is used to test the validity of Eq. (39) and to assess the importance generally of the long-range couplings.

We have used the variational adiabatic wave functions of Lin[22] to compute ground-state potential curves and the diagonal elements of the derivative matrix $W_{\mu\mu}(R)$ for the model Hamiltonian. The one-channel radial equation in R is then solved for the s-wave shift. Figure 1 compares the present adiabatic phase shifts with Hartree-Fock results of Ref. 5. Notice the good agreement for small k, but the increasing inaccuracy of the adiabatic phase shift with increasing k. The dot-dashed curve is the corrected phase shift using Eq. (39) with $R_0 = 6$ a.u. and $C = 3$ a.u. The agreement with the Hartree-Fock phase is significantly improved, but still not complete. The origin of the remaining discrepancy probably relates to uncertainties in the proper choice (Ref. 18) for R_0, since use of $R_0 = 4$ a.u. gives a phase shift indistinguishable from the Hartree-Fock. Accordingly, we conclude that the slow convergence of R to r_1 is the main source of error in the adiabatic model Hamiltonian calculations. Furthermore, the correction must apply to more complete adiabatic calculations.

We have applied this correction to the phase shifts of Lin[9] which incorporate the full electron-electron interaction in the adiabatic approximation. In this case the adiabatic functions do not necessarily assume their asymptotic form at $R = 6$ a.u., owing to the polarization of the H-atom wave functions. In the absence of better information, we continue to use $R_0 = 6$ a.u.

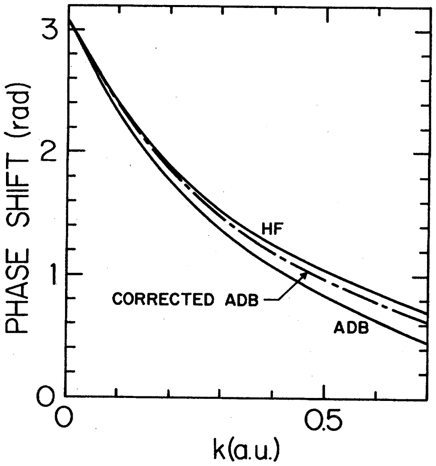

FIG. 1. ^1S-wave phase shifts in H^-. The curve labeled "ADB" represents the adiabatic phase shift calculated in the monopole approximation, while the curve labeled "HF" is the corresponding Hartree-Fock phase shift from Ref. 15. The dot-dashed curve is the adiabatic phase plus the asymptotic correction with $R_0 = 6$ a.u. With $R_0 = 4$ a.u. the corrected phase is indistinguishable from the Hartree-Fock result.

Table I lists the one- and two-channel phase shifts of Ref. 5. The two-channel phase at $k = 0.7$ a.u. is taken from Ref. 16. There are significant differences between the one- and two-channel results. To see if the long-range interactions account for these differences we have computed the contribution of the $n = 2$ channels to the sum for C_μ. We find the two $n = 2$ channels account for 55% of the sum. Using the A coefficients of Ref. 3 one then finds that the second channel contributes 40%. The sum of the adiabatic phase and $0.4C/R_0$ is given in column 2. Clearly, the long-range interaction does not account for the change in going from one to two channels. Substantial effects not related to the slow approach of R to r_1 must play a role.

The two-channel results also lie below the best calculated values of Schwartz.[23] According to our expression Eq. (30) for C_μ and the computed asymptotic contribution from the second channel, the states omitted in the two-channel calculation contribute $0.6k/R_0$ asymptotically. Column 4 of Table I lists the sum of the two-channel phase and this correction. The correction appears to account for the remaining discrepancy between the two-channel results and those of Schwartz.[23] This conclusion is somewhat tentative owing to the smallness of the correction and the uncertainty in R_0.

The phase-shift correction has been derived specifically for $l_{1\mu} = 0$ and $Z - 1 = 0$. Since the slow approach of R to r_1 is independent of angular momentum and charge, a similar correction applies to all partial waves and to all Z. Using the methods of Sec. II, it is relatively easy to show that, to first order in R, the corrections to the wave func-

TABLE I. One- and two-channel e^--H ^1S phase shifts from Refs. 9 and 16. The correction C is given by $C=3k/2R_0=0.25k$ for $R_0=6$ a.u.

k	One-channel	One-channel $+0.4C$	Two-channel	Two-channel $+0.6C$	Schwartz[a]
0.1	2.513	2.523	2.521	2.536	2.553
0.2	1.983	2.003	2.003	2.033	2.067
0.3	1.568	1.598	1.659	1.704	1.696
0.4	1.242	1.282	1.380	1.440	1.414
0.5	0.989	1.029	1.142	1.217	1.202
0.6	0.784	0.844	0.928	1.018	1.041
0.7	0.618	0.678	0.744	0.850	0.930

[a] Reference 23.

tion and the phase shifts hold independently of $l_{1\mu}$, L, and Z. One must recognize that the appropriate matching radius of the phase-shift correction R depends upon $l_{1\mu}$ and $Z-1$. This is easily seen since asymptotic solutions are valid only when the local wave number

$$k_\mu(R)=[k_\mu^2-l_{1\mu}(l_{1\mu}+1)/R^2+2(Z-1)/R]^{1/2} \tag{40}$$

can be expanded in inverse powers of R. Then, in addition to the requirement that R must be greater than or equal to some matching radius determined by the range where the couplings assume their asymptotic values, one must also have

$$R_0>[l_{1\mu}(l_{1\mu}+1)]^{1/2}/k_\mu \ , \tag{41}$$

and

$$R_0>(Z-1)/k_\mu^2 \ . \tag{42}$$

The conditions Eqs. (41) and (42) are needed to ensure the validity of the asymptotic expansion in the absence of coupling. Finally, we caution that our asymptotic solutions always require the condition $C_\mu k_\mu/2R_0 \ll 1$.

IV. DISCUSSION

The asymptotic solutions indicate a feature that must be corrected in the hyperspherical adiabatic basis of atomic states, namely more adequate representations of the independent particle modes of electron motion must be devised. This section evaluates the efficacy of applicable techniques.

One of the chief virtues of the adiabatic approximation is that a single, local, adiabatic potential $U_{\mu\mu}(R)$ characterizes an entire channel. Accordingly, we first consider transformations which preserve this feature. The diabatic transformation of Heil, Butler, and Dalgarno[24] has proved useful near avoided crossings. Although Heil *et al.* caution against its use for a complete set of equations, its values in the large-R region will be assessed.

The transformation matrix U which transforms from the adiabatic to the diabatic basis is a solution of the equations

$$\frac{dU_{\mu j}}{dR}=\sum_\nu P_{\mu\nu}(R)U_{\nu j} \ , \tag{43}$$

where

$$P_{\mu\nu}(R)=\left[\phi_\mu,\frac{\partial\phi_\nu}{\partial R}\right] . \tag{44}$$

For large R we have

$$\frac{dU_{\mu j}}{dR}=-\sum_\nu a_{\mu\nu}U_{\nu j}/R \ . \tag{45}$$

Setting $x=\ln R$ we have

$$\frac{dU_{\mu j}}{dx}=-\sum_\nu a_{\mu\nu}U_{\nu j} \ . \tag{46}$$

Since the elements $a_{\mu\nu}$ form a constant antisymmetric matrix, the solution of Eq. (39) is just

$$U_{\mu\nu}=U_{\mu j}(0)\exp(ia_j x)[U^{-1}(0)]_{j\nu} \ , \tag{47}$$

where ia_j, with a_j real, are the eigenvalues of the matrix $\|a_{\mu\nu}\|$, and $[U(0)]_{\mu j}$ are the elements of the corresponding eigenvectors. With this transformation the coupled equations in the diabatic basis contain coupling matrix elements M_{ij} of the form

$$M_{ij}=\text{const}\times\cos[(a_i-a_j)\ln R] \ . \tag{48}$$

Since the couplings do not vanish as $R\to\infty$, the diabatic basis is unsatisfactory at large R. This is not surprising in view of the discussion of Ref. 24 which emphasizes the applicability of the transformation near *sharp* changes in the adiabatic basis functions. In the present case the change is, on the contrary, quite gradual. Sharp changes do occur for smaller R. There the diabatic transformation is useful, but it cannot be applied over the entire range.

An interesting alternative is represented by the post-adiabatic transformation of Klar.[25] This approximation has been applied to the hyperspherical radial equations with favorable results.[11] Since its convergence properties at large R have not been assessed, it is pertinent to determine how well it represents the asymptotic region.

The post-adiabatic transformation seeks the eigenvalues $u_\mu(R)$ for a set of first-order equations equivalent[25] to the second-order equations Eq. (1). In the large-R limit it is convenient to use the local wave number $k_\mu(R)$ rather than the adiabatic potentials $U_{\mu\mu}(R)$ in the eigenvalue equation. With this change of notation and letting D_ν denote the elements of the post-adiabatic eigenvectors, Eq.

(14) of Ref. 25 reads, in the asymptotic region,

$$[u_\mu(R)+k_\mu^2]D_\mu = [4u_\mu(R)/R^2]\sum_{\nu,\nu'} a_{\mu\nu}a_{\nu\nu'}D_{\nu'}/[u_\mu(R)+k_\nu^2] \; . \qquad (49)$$

The zeroth-order approximation neglects the right-hand side of Eq. (49), which is of order $1/R^2$, entirely. The zeroth-order eigenvalues and eigenvectors are then given by

$$\begin{aligned} &u_\mu(R)=-k_\mu^2 \; , \\ &D_\mu=1 \; , \\ &D_\nu=0, \quad \nu\neq\mu \; . \end{aligned} \qquad (50)$$

Substituting the zeroth-order estimates into the right-hand side of Eq. (49) gives the first-order eigenvalue

$$\begin{aligned} u_\mu(R) &= -k_\mu^2-(4k_\mu^2/R^2)\sum_\nu [a_{\mu\nu}a_{\nu\mu}/(k_\nu^2-k_\mu^2)] \\ &= -k_\mu^2(1+C_\mu/R^2) \; , \end{aligned} \qquad (51)$$

where Eq. (31) has been used. Equation (51) is just Klar's[25] Eq. (16).

The asymptotic standing-wave functions corresponding to these eigenvalues are

$$F_\mu(R)\sim\sin\left[\int^R \sqrt{|u_\mu(R')|}\,dR'+\delta\right] \; . \qquad (52)$$

Again, note that δ is arbitrary and at our disposal. Recalling that $B_\mu=-k_\mu C_\mu/2$ and evaluating the integral in Eq. (52) we have

$$F_\mu(R)\sim\sin(k_\mu R+B_\mu/R+\delta) \; . \qquad (53)$$

Comparing Eqs. (19) and (53) shows that the post-adiabatic approximation to the phase shift incorporates the asymptotic solution exactly to order $1/R$. It thus represents a promising direction for further work. The main difficulty here is the need for a sufficiently large basis of adiabatic states to represent the constant B_μ accurately, as discussed in Sec. II.

The agreement between the post-adiabatic approximation and the asymptotic solutions is not surprising in view of the connection between the post-adiabatic transformation and the WKB approximation.[25] To the extent that couplings can be neglected after the transformation, the solutions just have the WKB form of Eq. (52). As is well known, the WKB approximation is valid in regions where there are no sharp changes, including reflections at a turning point. These conditions are met asymptotically, where the direct solutions and the post-adiabatic solutions agree. Alternatively, the lowest-order post-adiabatic approximation fails near sharp changes of potentials or couplings, such as occur near avoided crossings. Here the diabatic transformation is appropriate. The two transformations that we have discussed, the diabatic and the post-adiabatic transformations, are thus seen to be complementary.

V. CONCLUSIONS

We have solved the infinite set of coupled radial equations of the hyperspherical adiabatic representation of two-electron atomic states to first order in $1/R$. The solution takes the form of a correction to the adiabatic coordinate R such that, for large r_1 with r_2 fixed, R is replaced by $X=R-r_2^2/2R$. The variable X approaches r_1 two orders faster than does R. Associated with this correction to the wave function is a phase-shift correction $B_\mu C_\mu/2R$. Comparisons of corrected adiabatic phase shifts with more accurate calculations reveal that (1) essentially all discrepancies between the Hartree-Fock s-wave phase shifts of H^- and adiabatic phase shifts in the monopole approximation[18] are accounted for by the correction at large R, (2) the differences between one-channel and two-channel adiabatic phase shifts[9] reflect dynamical couplings not included in the large-R correction, and (3) the remaining discrepancies between the two-channel adiabatic phases and the best calculations of Schwartz[23] appear to be accounted for by the large-R correction.

ACKNOWLEDGMENT

Support for this research by the U.S. Department of Energy is gratefully acknowledged.

APPENDIX

Asymptotic solutions are valid only for sufficiently large R and are accordingly employed in scattering theory to match onto solutions valid in an inner region. Solutions in the inner region satisfy boundary conditions at $R=0$ while solutions in the asymptotic region satisfy boundary conditions at infinite R. There are two sets of solutions in the outer region, one set that varies as the sine function of some argument and one that varies as the cosine of the same argument. The general solution in the asymptotic region is a linear combination of the two solutions. The particular superposition of asymptotic solutions is determined by matching logarithmic derivatives of the inner and outer solutions at some matching radius R_0. Examination of the solutions thus obtained determines the K matrix. This procedure is formally developed in standard texts[15] but is reviewed here to illustrate a key point of our derivation of the phase-shift correction, namely that closed channels contribute only in second order. Actually, this follows immediately from the equation of Dalitz.[26] Our discussion therefore makes no pretense of originality and is presented here to illustrate explicitly the nature of the assumptions made in obtaining the phase-shift correction. All assumptions are consistent with the neglect of terms of order $1/R_0$ in the asymptotic solutions.

Because we deal with a multichannel problem, it is convenient to employ the matrix notation. To that end we define the matrices $\underline{f}$ and $\underline{g}$ of free-particle sine- and cosine-type solutions in a potential-free region,

$$\begin{aligned} f_{\mu\nu}(R) &= \sin(k_\mu R-l_{1\mu}\pi/2)\delta_{\mu\nu} \; , \\ g_{\mu\nu}(R) &= \cos(k_\mu R-l_{1\mu}\pi/2)\delta_{\mu\nu} \; . \end{aligned} \qquad (\mathrm{A1})$$

By setting $\delta=-l_{1\mu}\pi/2$ in our asymptotic solutions Eq. (19) we obtain sine-like solutions valid through order $1/R$:

$$\mathcal{F}_{\nu\mu}(R)=f_{\nu\mu}(R)+g_{\nu\nu}(R)A_{\nu\mu}/R\ . \tag{A2}$$

The two indices on $\mathcal{F}_{\nu\mu}$ have rather different meanings. The first index ν refers to the index summed over in forming the total wave function of Eq. (6) while the second index refers to the channel which contains the sine wave term. The diagonal matrix element $A_{\mu\mu}$ therefore equals B_μ of Sec. II while elements $A_{\nu\mu}$ with $\nu\neq\mu$ were denoted by A_ν in the text. Since some of the wave vectors k_μ may be purely imaginary corresponding to energetically closed channels, it will be understood that Eq. (A1) still applies but with $k_\mu=i\,|k_\mu|$ when $k_\mu^2<0$.

In matrix notation the sine-like solutions are written

$$\underline{\mathcal{F}}(R)=\underline{f}(R)+\underline{g}(R)\underline{A}/R\ . \tag{A3}$$

Similarly, by setting δ of Eq. (19) equal to $-l_{1\mu}\pi/2+\pi/2$ we obtain the linearly independent set of cosine-like solutions

$$\underline{\mathcal{G}}(R)=\underline{g}(R)-\underline{f}(R)\underline{A}/R\ . \tag{A4}$$

At large R the functions $\underline{\mathcal{F}}$ and $\underline{\mathcal{G}}$ go to the free-wave solutions, thus the general solution in the asymptotic region is given by

$$\underline{\mathcal{F}}(R)+\underline{\mathcal{G}}(R)\underline{K}\ , \tag{A5}$$

where $\underline{K}$ is the standard K matrix of scattering theory.

To determine $\underline{K}$ we must match to the logarithmic derivative matrix $\underline{L}(R_0)$ determined by the inner solution. The equation for $\underline{K}$ is then

$$\underline{L}(R_0)=[\underline{\mathcal{F}}'(R_0)+\underline{\mathcal{G}}'(R_0)\underline{K}][\underline{\mathcal{F}}(R_0)+\underline{\mathcal{G}}(R_0)\underline{K}]^{-1}\ . \tag{A6}$$

We now define a reaction matrix $\underline{K}^{(0)}=\underline{A}/R_0$ which pertains to the outer region only. To order $1/R_0$ we have

$$\begin{aligned}\underline{\mathcal{F}}(R_0)&=\underline{f}(R_0)+\underline{g}(R_0)\underline{K}^{(0)}\ ,\\ \underline{\mathcal{G}}(R_0)&=\underline{g}(R_0)-\underline{f}(R_0)\underline{K}^{(0)}\ ,\end{aligned} \tag{A7}$$

$$\begin{aligned}\underline{\mathcal{F}}'(R_0)&=\underline{f}'(R_0)+\underline{g}'(R_0)\underline{K}^{(0)}+O(1/R_0^2)\ ,\\ \underline{\mathcal{G}}'(R_0)&=\underline{g}'(R_0)-\underline{f}'(R_0)\underline{K}^{(0)}+O(1/R_0^2)\ .\end{aligned} \tag{A8}$$

Substituting Eqs. (A7) and (A8) into Eq. (A6) and defining $\underline{K}^{(i)}$ according to

$$\underline{K}^{(i)}=(\underline{K}+\underline{K}^{(0)})/(\mathbb{1}-\underline{K}^{(0)}\underline{K})\ , \tag{A9}$$

we have

$$\begin{aligned}\underline{L}(R_0)=&[\underline{f}'(R_0)+\underline{g}'(R_0)\underline{K}^{(i)}]\\ &\times[\underline{f}(R_0)+\underline{g}(R_0)\underline{K}^{(i)}]^{-1}\ .\end{aligned} \tag{A10}$$

Equation (A10) now has the form that obtains when the inner solutions are matched to free-wave solutions, rather than the more correct asymptotic solutions, at the boundary R_0. For that reason $\underline{K}^{(i)}$ is identified as the K matrix obtained without the correction for the long-range interactions. Equation (A9) relates $\underline{K}^{(i)}$ determined from the inner solution, $\underline{K}^{(0)}$ determined in the outer region, and the correct K matrix which incorporates the dynamics of both the inner and outer regions. Notice that Eq. (A9) has the form of the addition theorem for the tangent of the difference of two angles. This becomes more apparent when Eq. (A9) is solved for the full K matrix $\underline{K}$:

$$\underline{K}=(\underline{K}^{(i)}-\underline{K}^{(0)})/(\mathbb{1}+\underline{K}^{(i)}\underline{K}^{(0)})\ . \tag{A11}$$

The final task is to introduce the assumptions of Sec. III used to obtain the phase-shift correction. Our first assumption is that the adiabatic approximation holds in the inner region so that the coupling between channels in that region is neglected. Then $\underline{L}(R_0)$ and consequently $\underline{K}^{(i)}$ are both diagonal with $K_{\mu\mu}^{(i)}$ equal to the tangent of the adiabatic phase shift:

$$K_{\mu\mu}^{(i)}=\tan\delta_\mu^{(\text{adb})}\ . \tag{A12}$$

Our next assumption is that, consistent with the order to which our asymptotic solutions have been obtained, terms of order $1/R_0^2$ are negligible. We now show that terms of order $1/R_0$ on the diagonal of $\underline{K}^{(0)}$ contribute to the phase shift to that order, but that nondiagonal terms do not. To that end we write $\underline{K}^{(0)}$ as the sum of a diagonal term $(\underline{K}^{(0)})_d$ and a term $(\underline{K}^{(0)})_n$ with only nondiagonal elements,

$$\underline{K}^{(0)}=(\underline{K}^{(0)})_d+(\underline{K}^{(0)})_n\ , \tag{A13}$$

and evaluate $\underline{K}$ to order $1/R_0$. One finds

$$\begin{aligned}\underline{K}\approx&[\underline{K}^{(i)}-(\underline{K}^{(0)})_d][\mathbb{1}+\underline{K}^{(i)}(\underline{K}^{(0)})_d]^{-1}\\ &-(\mathbb{1}+\underline{K}^{(i)})(\underline{K}^{(0)})_n\ .\end{aligned} \tag{A14}$$

The first term of Eq. (A14) is diagonal and the second has only nondiagonal elements. This expression is then used in the equation for the S matrix to obtain S-matrix elements and phase shifts. Equivalently, one computes the reduced K matrix of Dalitz.[26] That is, if we partition the K matrix into four blocks, $\underline{K}_{oo}$, $\underline{K}_{oc}$, $\underline{K}_{co}$, and $\underline{K}_{cc}$, the reduced K matrix $\overline{\underline{K}}_{oo}$ is given by

$$\overline{\underline{K}}_{oo}=\underline{K}_{oo}+i\underline{K}_{oc}(\mathbb{1}+i\underline{K}_{cc})^{-1}\underline{K}_{co}\ . \tag{A15}$$

This equation is usually used for the case where the K matrix is partitioned into open channels o and closed channels c but actually holds for any partitioning.[26] When some of the channels c are energetically open, the reduced K matrix is complex reflecting the complex phase needed to account for flux loss to the open channels included in the group c. In the present application the c represents all other channels, open or closed. Since the nondiagonal elements $K_{\mu\nu}$ are of order $1/R_0$ the second term in Eq. (A15) is of order $1/R_0^2$ and may be neglected. The corrected, diagonal K matrix is then given by

$$\overline{\underline{K}}\approx[\underline{K}^{(i)}-(\underline{K}^{(0)})_d][\mathbb{1}+\underline{K}^{(i)}(\underline{K}^{(0)})_d]^{-1}\ . \tag{A16}$$

Because Eq. (A16) has the form of the addition theorem for the tangent of the two angles, it follows that

$$\delta_\mu^{(c)}=\delta_\mu^{(\text{adb})}-A_{\mu\mu}/R_0+O(1/R_0^2)\ . \tag{A17}$$

Recalling the definition of $A_{\mu\mu}$, we see that Eq. (A17) is equivalent to Eq. (36) of Sec. III.

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