Symmetric two-center problem: interpolation solution

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A one-electron diatomic molecule with identical nuclei is examined in the Born-Oppenheimer approximation. The well-known method for separating variables in the Schrödinger equation for this problem is used. A new mathematical representation of a solution of this problem is proposed. The characteristics of the solution are calculated by an iterative method. Closed expressions describing the electron energy as a function of the distance R between nuclei are constructed in this manner in a first approximation. Exact values of the energy are found in the limiting cases in which R vanishes or increases without bound. These relations can thus be thought of as interpolations. The second-approximation correction to the energy is derived for the ground state and the first excited state. A numerical comparison is made of the results of the present paper and the exact solution of the problem.

The quantum-mechanical description of a one-electron diatomic molecule (e.g., the molecular hydrogen ion H_2^+) is based on the Born-Oppenheimer approximation or the two-center problem,[1-4] in which bound states of the electron are examined in the field of two fixed positive charges separated by a distance R. A distinctive and obvious feature of this problem is that the wave functions and energies of the electron depend on the distance R; the dependence is of such a nature that in the two limiting cases $R = 0$ (the combined atom) and an infinitely increasing separation (separate nuclei) one obtains the wave functions and energy spectrum of the hydrogen atom or of a hydrogen-like atom. Strict correspondence rules hold between the electron states in each of these limits. These rules are based on general principles, so they can be determined without solving the Schrödinger equation of the two-center problem and without determining the wave functions and energies of the electron for intermediate values of R (Refs. 2 and 5).

These comments suggest that it might be possible to construct an approximate solution of the two-center problem which would become the exact solution in each of these limiting cases. It turns out that this idea can be implemented to a certain extent; a description of an approximate solution of this sort is the basic content of the present paper.

A brief preliminary report of the results of this study was published recently.[6]

1. LIMITING STATES OF A TWO-CENTER SYSTEM AND CORRESPONDENCE RULES BETWEEN THEM

Variables are separated in the Schrödinger equation for the two-center problem[1,3] by transforming to the so-called coordinates of a prolate ellipsoid of revolution:

$$\xi = \frac{r_1 + r_2}{R}, \qquad 1 \leqslant \xi < \infty, \tag{1}$$

$$\eta = \frac{r_1 - r_2}{R}, \qquad -1 \leqslant \eta \leqslant 1, \tag{2}$$

$$\varphi, \quad 0 \leqslant \varphi \leqslant 2\pi. \tag{3}$$

Here r_1 and r_2 are the distances from the electron to the first and second centers, respectively, and φ is the angular position around the axis passing through the centers.

In the limit as R vanishes, the coordinates in (1)–(3) become spherical coordinates:

$$\frac{1}{2} R\xi \approx r, \qquad \eta \approx \cos\theta, \qquad R \ll 1. \tag{4}$$

In the opposite limit in which R increases without bound, we obtain parabolic coordinates:

$$R(\xi - 1) \approx \lambda_{1,2}, \qquad R(1 \pm \eta) \approx \mu_{1,2}, \qquad R \gg 1. \tag{5}$$

The subscripts 1 and 2 correspond to the choice of the focus of the parabolic coordinate system at the first and second centers, respectively.

Taking these limiting properties of coordinates (1)–(3) into account, we will discuss the hydrogen-like "combined" atom in spherical coordinates, while we will discuss the hydrogen atom in the limit of "separated" nuclei in parabolic coordinates. As is known,[7] the variables can be separated in the Schrödinger equation for the hydrogen atom or for a hydrogen-like atom in either case.

For convenience in the discussion below, we will gather here for reference the known expressions for the wave functions and energies of the bound states in both coordinate systems. All the expressions, here and below in this paper, will be written for the molecular hydrogen ion H_2^+ (or D_2^+). The transformation to the more general case presents no difficulties, but we do not need to go through it.

The bound states of the combined atom (He^+) in spherical coordinates are characterized by the quantum numbers n, l, m, and the wave functions and energies of the states are described by[2,7]

$$\Psi(r, \theta, \varphi) \sim X(r) Y(\cos\theta) e^{\pm im\varphi}, \tag{6}$$

$$X(r) = e^{-r_n/2} r_n{}^l L_{n-l-1}^{2l+1}(r_n), \qquad r = 4r/n, \tag{7}$$

$$Y(\cos\theta) = \mathscr{P}_l{}^m(\cos\theta), \tag{8}$$

$$E = -2/n^2, \tag{9}$$

$$m = 0, 1, 2, \ldots; \quad l = m, m+1, \ldots; \quad n = l+1, l+2, \ldots, \tag{10}$$

where $L_{n-l-1}^{2l+1}(r_n)$ is a generalized Laguerre polynomial, and $\mathscr{P}_l{}^m(\cos\theta)$ is the associated Legendre function of type I.

The bound states of the hydrogen atom in parabolic coordinates are characterized by the numbers N, K, m; the corresponding relations for the wave functions and energies are[2,5]

$$\Psi(\lambda, \mu, \varphi) \sim X(\lambda) Y(\mu) e^{\pm im\varphi}, \tag{11}$$

$$X(\lambda) = e^{-\lambda_N/2} \lambda_N^{m/2} L_{N-K-m-1}^m (\lambda_N), \quad \lambda_N = \lambda/N, \tag{12}$$

$$Y(\mu) = e^{-\mu_{1N}/2} \mu_{1N}^{m/2} L_K^m (\mu_{1N}) \pm e^{-\mu_{2N}/2} \mu_{2N}^{m/2} L_K^m (\mu_{2N}),$$

$$\mu_N = \mu/N, \tag{13}$$

$$E = -1/2N^2, \tag{14}$$

$$m = 0, 1, 2, \ldots; \quad K = 0, 1, 2, \ldots; \quad N = K+m+1, K+m+2, \ldots \tag{15}$$

The choice of sign in (13) determines the parity of the state. The coordinates μ_1 and μ_2 can be expressed in terms of η with the help of (5).

The correspondence between states (6)–(9) and (11)–(14) in the case of a symmetric two-center system can be determined on the basis of the conservation of the number of zeros of a wave function along each coordinate as the parameter R is varied.[2,5] We will call the numbers which determine the number of zeros of the wave function along some coordinate or other the "node quantum numbers," and we will denote them by n_ξ, n_η, n_φ, as in Ref. 2. These numbers remain the same for a given state of a symmetric two-center system at all values of R, from zero to infinity, but for the limiting states (6)–(9) and (11)–(14) they can be determined easily by working from the well-known properties of the trigonometric functions, the Laguerre polynomials, and the associated Legendre functions which appear in the expressions for the wave functions. We thus find from (6)–(9) and (11)–(14)

$$n_\xi = n - l - 1 = N - K - m - 1, \tag{16}$$

$$n_\eta = l - m = \begin{cases} 2K, \\ 2K+1, \end{cases} \tag{17}$$

$$n_\varphi = m. \tag{18}$$

According to these relations, the quantum numbers n, l, and m of the combined atom determine the quantum numbers N, K, and m, so they can be used to label the states of the two-center system at arbitrary R (Ref. 8).

2. EXACT SOLUTION

The solution proposed here for the two-center problem is closely related to known exact solutions of this problem,[9,10] so we will briefly review the basic characteristics of those solutions here. A more detailed account can be found in Refs. 1 and 3, among other places.

If we transform to coordinates (1)–(3) in the Schrödinger equation for a one-electron diatomic molecule in the Born-Oppenheimer approximation, and if we substitute the product

$$\Psi(\xi, \eta, \varphi) \sim X(\xi) Y(\eta) e^{\pm im\varphi}, \quad m = 0, 1, 2, \ldots, \tag{19}$$

into this equation as a wave function, we find the following differential equations for the functions $X(\xi)$ and $Y(\eta)$ in our case of identical unit nuclear charges:

$$\frac{\partial}{\partial \xi} (\xi^2 - 1) \frac{\partial}{\partial \xi} X(\xi) + \left[-C + 2R\xi - p^2(\xi^2 - 1) - \frac{m^2}{\xi^2 - 1} \right] X(\xi) = 0, \tag{20}$$

$$\frac{\partial}{\partial \eta} (1 - \eta^2) \frac{\partial}{\partial \eta} Y(\eta) + \left[C - p^2(1 - \eta^2) - \frac{m^2}{1 - \eta^2} \right] Y(\eta) = 0, \tag{21}$$

$$p = R \left(-\frac{1}{2} E \right)^{1/2}. \tag{22}$$

Here C is the constant of the separation of variables, and E is the energy of the electron.

The results of this study were found through an analysis of Eq. (20). Equation (21) is the same as the equation for angular spheroidal functions in the coordinates of an oblate ellipsoid of revolution; information about its solutions can be found in Refs. 3 and 11. For the problem at hand, we are of course interested in that solution of Eq. (21) which is the same as (8) in the limit $R = 0$. That solution is related to the definition of the separation constant C as a function of the parameter p in (22) and the integers l and m:

$$C \equiv C(l, m, p). \tag{23}$$

These integers are the same as the corresponding quantum numbers in (10) of the combined atom. From the mathematical standpoint, the number l is the index of a branch of a multivalued function. Definition (23) has the following limits:[11]

$$\lim_{p \to 0} C(l, m, p) = l(l+1), \tag{24}$$

$$\lim_{p \to \infty} \frac{C(l, m, p)}{2p} = 2K + m + 1. \tag{25}$$

The number K on the right side of (25) is the same as the "parabolic" quantum number in (15).

An exact physically meaningful solution of Eq. (20) was derived[9,10] back in the early 1930s in two equivalent representations. In each case, the unknown function was first put in the form

$$X(s) \propto e^{-s/2} s^{m/2} (s + 4p)^{m/2} u(s), \tag{26}$$

$$s = 2p(\xi - 1), \quad 0 \leqslant s < \infty. \tag{27}$$

Here and below, we will use the variable s instead of ξ, because in the limit $R = 0$ it becomes the same as the variable r_n in (7), while as R increases without bound it becomes the variable λ_N in (12).

The following expansion of the function $u(s)$ in (26) is the most convenient one for practical calculations:[10]

$$u(s) \propto (s + 4p)^\sigma \sum_{j=0}^{\infty} a_j^{nlm} \left(\frac{s}{s + 4p} \right)^j. \tag{28}$$

Another representation[9] of $u(s)$,

$$u(s) \infty \sum_{j=0}^{\infty} a_j^{nlm} L_j^m(s), \qquad (29)$$

is more convenient for finding the asymptotic behavior of $X(s)$ at $R \gg 1$ (Ref. 2), since the Laguerre polynomials in (29) are of the same type (in terms of the superscript) as in (12).

The parameter σ in (28) is related to R and E by

$$R = p(\sigma + m + 1), \qquad (30)$$

$$E = -\frac{2}{(\sigma + m + 1)^2}. \qquad (31)$$

The coefficients a_j^{nlm} in (28) and (29) satisfy equivalent three-term relations. These three-term relations generate a transcendental equation which establishes the relationship among σ, p, C, and m. Along with (23), it thus determines the behavior of the parameter σ as a function of the parameter p and of the three integers n, l, and m, which are the same as the quantum numbers of the combined atom in (10):

$$\sigma \equiv \sigma(n, l, m, p). \qquad (32)$$

This functional dependence, along with (30) and (31), determines E as a function of R either parametrically through the parameter p or directly, if the latter is eliminated with the help of (22). It is important to note, however, that the transcendental equation which we just mentioned does not determine the functional dependence (32) explicitly. In practice, this functional dependence can be found either numerically, in the form of tables,[12-14] or in the form of asymptotic expansions for small[15,16] or large[2] values of R. This comment also applies to the determination of the coefficients a_j^{nlm} in (28) and (29).

3. SOLUTION OF THE INTERPOLATION TYPE

In this paper we propose and analyze a new representation of the function $u(s)$ in (26). This representation is

$$u(s) \propto (s+4p)^{\varkappa} \sum_{j=0}^{\infty} c_j L_j^{2l+1}(s) \equiv (s+4p)^{\varkappa} v(s). \qquad (33)$$

The Laguerre polynomials in this expansion are of the same type in terms of the superscript as those in (7), so representation (33) is in a sense symmetric with respect to representation (29). There is the hope that this representation will be convenient for an approximate description of the solution of the two-center problem at small values of R. As the discussion below demonstrates, this hope is justified.

Unfortunately, three-term relations cannot be found for the coefficients c_j in (33). To determine them and also the dependence of E on R, we accordingly use an iterative method developed for the purpose. We first substitute (26) and (27) with $u(s)$ from (33) into Eq. (20). We thereby transform it into the following equation for the function $v(s)$:

$$sv'' + [2(l+1) - s]v' + (\sigma - \sigma^{(0)} + n_{\xi})v$$
$$= \left[-2(\varkappa - n_{\eta}) + \frac{4p(2\varkappa + m + 1)}{s + 4p} \right] v'$$
$$+ \left[\varkappa - n_{\eta} - \frac{\varepsilon}{s + 4p} + \frac{4p\varkappa(\varkappa + m)}{s + 4p} + \frac{4p\varkappa(\varkappa + m)}{(s + 4p)^2} \right] v, \qquad (34)$$

where

$$\sigma^{(0)} = \lim_{p \to 0} \sigma = n - m - 1 = n_{\xi} + n_{\eta}, \qquad (35)$$

$$\varepsilon = (1 + 4p)\varkappa^2 + (2m + 1)(1 + 2p)\varkappa - 2p(\sigma - \varkappa) - C + m(m + 1). \qquad (36)$$

We now multiply Eq. (34) by $e^{-s} s^{2l+1} L_\nu^{2l+1}(s)$, $\nu = 0, 1, 2,...$ and integrate it over s from zero to infinity. Then substituting the sum over Laguerre polynomials from (33) in place of $v(s)$ in the integrand on the left side, and using the orthogonality relations for these polynomials, we find the following system of equations:

$$(\sigma - \sigma^{(0)} + n_{\xi} - \nu)c_\nu$$

$$= \frac{\nu!}{(\nu + 2l + 1)!} \int_0^{\infty} ds\, e^{-s} s^{2l+1} L_\nu^{2l+1}(s)$$

$$\times \left\{ \left[-2(\varkappa - n_\eta) + \frac{4p(2\varkappa + m + 1)}{s + 4p} \right] v'(s) \right.$$

$$\left. + \left[\varkappa - n_\eta - \frac{\varepsilon}{s + 4p} + \frac{4p\varkappa(\varkappa + m)}{s + 4p} + \frac{4p\varkappa(\varkappa + m)}{(s + 4p)^2} \right] v(s) \right\},$$

$$\nu = 0, 1, 2, ... \quad . \qquad (37)$$

We will solve this system of equations, i.e., determine σ and c_ν as functions of the parameter p and the quantum numbers n, l, and m, by an iterative method. We set

$$\sigma = \sigma^{(0)} + \sigma^{(1)} + \sigma^{(2)} + \dots,$$

$$c_\nu = c_\nu^{(0)} + c_\nu^{(1)} + c_\nu^{(2)} + \dots; \quad \nu = 0, 1, 2, \dots; \quad c_{n_\xi}^{(0)} = 1;$$

$$c_\nu^{(0)} = 0; \quad \nu \neq n_\xi.$$

In the first step of the iterative process, we thus substitute $L_{n_\xi}^{2l+1}(s)$ for $v(s)$ on the right side of (37). Using next the orthogonality relations and introducing some new notation for the integrals,

$$f'(\nu, n_\xi, 2l + 1, 4p)$$

$$= \frac{\nu! 4p}{(\nu + 2l + 1)!} \int_0^{\infty} \frac{ds\, e^{-s} s^{2l+1}}{s + 4p} L_\nu^{2l+1}(s) \frac{d}{ds} L_{n_\xi}^{2l+1}(s), \qquad (38)$$

$$f_1(\nu, n_\xi, 2l + 1, 4p)$$

$$= \frac{\nu! 4p}{(\nu + 2l + 1)!} \int_0^{\infty} \frac{ds\, e^{-s} s^{2l+1}}{s + 4p} L_\nu^{2l+1}(s) L_{n_\xi}^{2l+1}(s), \qquad (39)$$

$$f_2(\nu, n_\xi, 2l + 1, 4p)$$

$$= \frac{\nu! 4p}{(\nu + 2l + 1)!} \int_0^{\infty} \frac{ds\, e^{-s} s^{2l+1}}{(s + 4p)^2} L_\nu^{2l+1}(s) L_{n_\xi}^{2l+1}(s), \qquad (40)$$

we find the equations

$$\sigma^{(0)}+\sigma^{(1)}=n_{\mathfrak{k}}+\varkappa+(2\varkappa+m+1)f'(n_{\mathfrak{k}},n_{\mathfrak{k}},2l+1,4p)$$

$$-\frac{\varepsilon}{4p}f_{1}(n_{\mathfrak{k}},n_{\mathfrak{k}},2l+1,4p)$$

$$+\varkappa(\varkappa+m)[f_{1}(n_{\mathfrak{k}},n_{\mathfrak{k}},2l+1,4p)+f_{2}(n_{\mathfrak{k}},n_{\mathfrak{k}},2l+1,4p)],\tag{41}$$

$$(n_{\mathfrak{k}}-v)c_{v}^{(1)}=2(\varkappa-n_{\eta})+(2\varkappa+m+1)f'(v,n_{\mathfrak{k}},2l+1,4p)$$

$$-\frac{\varepsilon}{4p}f_{1}(v,n_{\mathfrak{k}},2l+1,4p)+\varkappa(\varkappa+m)$$

$$\times[f_{1}(v,n_{\mathfrak{k}},2l+1,4p)+f_{2}(v,n_{\mathfrak{k}},2l+1,4p)],$$

$$v<n_{\mathfrak{k}},\tag{42}$$

$$(n_{\mathfrak{k}}-v)c_{v}^{(1)}=(2\varkappa+m+1)f'(v,n_{\mathfrak{k}},2l+1,4p)$$

$$-\frac{\varepsilon}{4p}f_{1}(v,n_{\mathfrak{k}},2l+1,4p)$$

$$+\varkappa(\varkappa+m)[f_{1}(v,n_{\mathfrak{k}},2l+1,4p)+f_{2}(v,n_{\mathfrak{k}},2l+1,4p)],$$

$$v>\eta_{\xi}.\tag{43}$$

These equations determine the solution of Eqs. (37) in a first approximation.

At this point the parameter $\varkappa$ is still arbitrary. We will erase this arbitrariness by a method which will be justified by the result. We substitute $\sigma^{(0)}+\sigma^{(1)}$ for σ in (36), and we equate the entire expression to zero. In place of (41) we then find two equations, for $\varkappa$ and $\sigma^{(0)}+\sigma^{(1)}$. Eliminating $\sigma^{(0)}+\sigma^{(1)}$, we find a quadratic equation in $\varkappa$:

$$[1+4p-2p(f_{1}+f_{2})]\varkappa^{2}$$

$$+[(2m+1)(1+2p)-4pf'-2mp(f_{1}+f_{2})]\varkappa$$
$$-C+m(m+1)-2n_{\mathfrak{k}}p-2(m+1)pf'=0.\tag{44}$$

The positive solution of this equation is

$$\varkappa=\frac{(2m+1)(1+2p)-4pf'-2mp(f_{1}+f_{2})}{2[1+4p-2p(f_{1}+f_{2})]}$$

$$\times\left\{\left[1+(C-m(m+1)+2n_{\mathfrak{k}}p+2(m+1)pf')\right.\right.$$
$$\left.\left.\times\frac{4[1+4p-2p(f_{1}+f_{2})]}{[(2m+1)(1+2p)-4pf'-2mp(f_{1}+f_{2})]^{2}}\right]^{\frac{1}{2}}-1\right\}.\tag{45}$$

The values of $\varkappa$ calculated from this expression can then be used to calculate $\sigma^{(0)}+\sigma^{(1)}$, from

$$\sigma^{(0)}+\sigma^{(1)}=n_{\mathfrak{k}}+\varkappa+(2\varkappa+m+1)f'+\varkappa(\varkappa+m)(f_{1}+f_{2}).\tag{46}$$

The latter relation was derived from (41) by equating ε to zero. The functions f',f_{1},f_{2} in (44)–(46) are taken with the same arguments as in (41). Equations (45) and (46), along with (30) and (31), determine the dependence of the electron energy E on R, parametrically through the parameter p, in the first approximation of our iterative method.

We can show that the limiting values of the energy calculated in this manner are exact. For this purpose we first find the limiting values of the functions f',f_{1},f_{2} with the help

of (38)–(40). We obviously have

$$f'(v,n_{\mathfrak{k}},2l+1,0)=f_{1}(v,n_{\mathfrak{k}},2l+1,0)=f_{2}(v,n_{\mathfrak{k}},2l+1,0)=0,$$
$$v=0,1,2,\dots\ .\tag{47}$$

As the parameter p increases without bound, we find, making use of the orthogonality relations,

$$\lim_{p\to\infty}f'(v,n_{\mathfrak{k}},2l+1,4p)=\begin{cases}-1,&v<n_{\mathfrak{k}},\\0,&v\geqslant n_{\mathfrak{k}},\end{cases}\tag{48}$$

$$\lim_{p\to\infty}f_{1}(v,n_{\mathfrak{k}},2l+1,4p)=\begin{cases}1,&v=n_{\mathfrak{k}},\\0,&v\neq n_{\mathfrak{k}},\end{cases}\tag{49}$$

$$\lim_{p\to\infty}f_{2}(v,n_{\mathfrak{k}},2l+1,4p)=0.\tag{50}$$

Substituting these limiting values along with (24) and (25) into (45), we find the following values of $\varkappa$:

$$\varkappa(n,l,m,0)=l-m=n_{\eta},\tag{51}$$

$$\lim_{p\to\infty}\varkappa(n,l,m,4p)=\frac{m+1}{2}\left\{\left[1+\frac{4(n_{\mathfrak{k}}+2K+m+1)}{(m+1)^{2}}\right]^{\frac{1}{2}}-1\right\}.\tag{52}$$

Substituting (51) along with (47) into (46), we find exact relation (35). Substituting (52) along with (48)–(50) into (46), we find the limiting value

$$\lim_{p\to\infty}(\sigma^{(0)}+\sigma^{(1)})=2n_{\mathfrak{k}}+2K+m+1=2N-m-1.\tag{53}$$

By virtue of (31) and (14), this limiting value is also the same as the exact value of σ in this limit.

Equations (45) and (46) therefore determine the exact limiting values of the parameter σ and thus, according to (31), those of the electron energy E. For this reason, these relations may be thought of as interpolation relations. The results calculated from (45) and (46) for the ground state and for the first three excited states of the molecular hydrogen ion H_{2}^{+} are shown in Table I and also in Figs. 1 and 2. These results give an idea of the accuracy of this interpolation.

Let us discuss certain aspects of calculations from (45) and (46). We first note that the separation constant C in (23) is assumed to be a known function of l, m, and p; corresponding values of this constant can be found in the tables of Refs. 12 and 13. Alternatively, they can be calculated from the formulas given in a handbook.[11] The volume of calculations remaining to be carried out is determined by the functions f',f_{1},f_{2} (with $v=n_{\xi}$), and it should increase with increasing n_{ξ}, as can be seen from the definitions of these functions in (38)–(40). It is useful in this connection to divide the entire set of states nlm into classes characterized by the node quantum number n_{ξ} in (16): $n_{\xi}=0$, $n_{\xi}=1$, etc. In particular, for the first two of these classes of this series, the functions f' and $f_{1}+f_{2}$, which appear in (45) and (46), take the following form, which is convenient for calculations:

$$n_{\mathfrak{k}}=0,\ f'=0,\ f_{1}+f_{2}=g_{2l}(4p),$$
$$n_{\mathfrak{k}}=1,\ f'=g_{2l+2}(4p)-g_{2l+1}(4p),\tag{54}$$

$$f_{1}+f_{2}=(2l+3)g_{2l+2}(4p)-4(l+1)g_{2l+1}(4p)+2(l+1)g_{2l}(4p).\tag{55}$$

TABLE I. Energies of the $1s\sigma_g$ ground state.

R	$-E_{ex}$	$-E_a$	$-E_i^{(1)}$	$-E_i^{(2)}$
0,1	1,9782421 *	1,9782028	1,9782644	
0,2	1,928705	1,9269071	1,9289279	
0,4	1,800785	1,7409152	1,8030927	
0,6	1,671505	1,2657404	1,6771397	
0,8	1,554475	0,1470958	1,563644	
1,0	1,45178		1,4640673	1,45576
2,0	1,102625		1,1231387	1,10824
3,0	0,91089		0,9328129?	
4,0	0,79608		0,81724634	
5,0	0,72442		0,74420522	0,728473
7,0	0,64845		0,66536752	
9,0	0,612305		0,62684948	0,614541
12,0	0,58350164 **		0,59542646	
20,0	0,55001426 **		0,5580098	
30,0	0,53333612 **		0,53898294	

Notation: E_{ex}—Exact solution; E_a—asymptotic expansion at small R (Ref. 15); $E_i^{(1)}$—interpolation solution, first approximation; $E_i^{(2)}$—interpolation solution, second approximation.

*From Ref. 13.
**From Ref. 14; the other data in this column are from Ref. 12.

The functions $g_k(4p)$, $k = 0, 1, 2,...$, are determined from

$$g_k(4p) = \frac{4p}{k!} \int_0^\infty \frac{ds\,e^{-s}s^k}{s+4p} = (4p)^{k+1}U(k+1, k+1, 4p),$$

(56)

where $U(a, b, z)$ is the second solution of the confluent hypergeometric equation.[11] The expansion of this function in powers of z contains $\ln z$ at integer values of the parameter b, so we conclude from (46) and (31) that the dependence of the electron energy on R will contain singularities of the $R^\delta \ln R$ type with integer values of δ at small values of R. In particular, the first term of this type for the ground state is $R^5 \ln R$, in agreement with a result from Ref. 15. Note also that there is a representation of function (56) in terms of a continuous fraction which is convenient for calculations.[17]
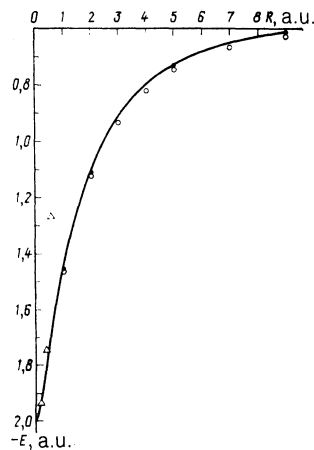
In a first approximation, the coefficients c_j of expansion (33) are calculated from (42) and (43), where ε should be set equal to zero. For $\varkappa$ and the functions f', f_1, and f_2, we should use expressions (45) and (38)–(40), respectively. The partitioning of the states nlm into classes on the basis of the node quantum number n_ξ in (16) is still meaningful. The volume of calculations increases with n_ξ. In the simplest case, $n_\xi = 0$, we find the following integral representation for $c_\nu^{(1)}$ from (43):

$$c_\nu^{(1)} = -\varkappa(\varkappa+m)\frac{(\nu-1)!}{(\nu+2l)!}4p\,G_\nu^{(2l)}(4p),$$

$$\nu = 1, 2, \ldots, \qquad n_\xi = 0,$$

(57)

$$G_\nu^{(k)} = \int_0^\infty \frac{ds\,e^{-s}s^{\nu+k}}{(s+4p)^{\nu+1}} = (\nu+k)!(4p)^k U(\nu+k+1, k+1, 4p),$$
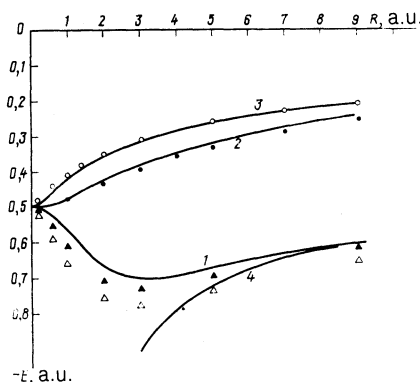
$$k = 0, 1, \ldots,$$

(58)

FIG. 1. Energy of the $1s\sigma_g$ ground state of the two-center system with identical unit charges at the centers as a function of the distance R between the centers. Solid line—exact solution constructed from the tables of Ref. 12; points—results calculated from the expressions given in the text proper for the interpolation solution. $\bigcirc$) First approximation; $\bullet$) second approximation; $\triangle$) asymptotic expansion from Ref. 15.

FIG. 2. The same as in Fig. 1, for the first three excited states. 1—$2p\sigma_u$; $\triangle$—first approximation; $\blacktriangle$—second approximation; curve 2—$2p\pi_u$; $\bullet$—first approximation; 3—$2s\sigma_g$; $\bigcirc$—first approximation; solid line 4—ground state.

where $U(a, b, 4p)$ is, as in (56), the second solution of the confluent hypergeometric equation.

With increasing index ν, the integral in (58) obviously decreases; it does so more rapidly, the greater the value of $4p$. For successive calculations of the quantities $G_\nu^{(k)}$, $\nu = 1$, $2,...$, the following relations are useful:

$$G_1 \ (4p) = \frac{k!}{4p} [k+1-(k+1+4p)(1-g_k)]$$
$$= (k-1)! [(k+1+4p)(1-g_{k-1})-k], \quad (59)$$

$$G_{\nu+1}^{(k)}(4p) = G_\nu^{(k)}(4p)\left[1-4p \int_0^\infty \frac{ds\,e^{-s}s^{\nu+k}}{(s+4p)^{\nu+2}} \Big/ \int_0^\infty \frac{ds\,e^{-s}s^{\nu+k}}{(s+4p)^{\nu+1}}\right].$$
$$(60)$$

The ratio of integrals can be expressed and calculated in terms of a continuous fraction,[17] and g_k in (59) is the same as in (56).

The limiting properties of the coefficients $c_\nu^{(1)}$ at small and large values of p, for arbitrary quantum numbers n, l, m, can easily be derived from (42) and (43) with the help of (47)–(50). The results are

$$\lim_{p\to 0} c_\nu^{(1)} = 0, \quad \nu \neq n_\xi, \qquad (61)$$

$$\lim_{p\to\infty} c_\nu^{(1)} = -\frac{2l+1-m}{n_\xi-\nu}, \quad \nu<n_\xi, \quad \lim_{p\to\infty} c_\nu^{(1)} = 0, \quad \nu>n_\xi.$$
$$(62)$$

4. SECOND-APPROXIMATION CORRECTION TO THE ELECTRON ENERGY

Going back to Eqs. (37), we now set $\sigma \approx \sigma^{(0)} + \sigma^{(1)} + \sigma^{(2)}$, and we replace $v(s)$ in the integrand on the right side by the sum of the zeroth and first approximations for this function:

$$v(s) \approx v^{(0)}(s) + v^{(1)}(s) = L_{n_\xi}^{2l+1}(s) + \sum_{\nu\neq n_\xi} c_\nu^{(1)} L_\nu^{2l+1}(s). \quad (63)$$

Using (36), we also set

$$\varepsilon = -2p\sigma^{(2)}. \qquad (64)$$

The definition of $\varkappa$ by means of (45) then remains in force.

As a result, after certain transformations, we find the following expression for the second-approximation correction to σ:

$$\sigma^{(2)} = \left[1 - \frac{1}{2}f_1(n_\xi, n_\xi, 2l+1, 4p)\right]^{-1} \left\{-(2l+1-m)\sum_{\nu=n_\xi+1}^\infty c_\nu^{(1)}\right.$$

$$+ (2\varkappa+m+1)\frac{n_\xi!}{(n_\xi+2l)!}$$

$$\times \sum_{\nu\neq n_\xi} c_\nu^{(1)} \frac{(\nu+2l+1)!}{\nu!4p} [f_1(\nu, n_\xi, 2l+1, 4p)$$

$$-f_1(\nu, n_\xi-1, 2l+1, 4p)] + (\varkappa+1)(\varkappa+m+1)\frac{n_\xi!}{(n_\xi+2l+1)!}$$

$$\times \sum_{\nu\neq n_\xi} c_\nu^{(1)} \frac{(\nu+2l+1)!}{\nu!} [f_1(\nu, n_\xi, 2l+1, 4p)$$

$$\left. + f_2(\nu, n_\xi, 2l+1, 4p)]\right\}. \qquad (65)$$

If $n_\xi = 0$, the second term in the second sum vanishes. Using (47)–(50), (61), and (62), we find

$$\lim_{p\to 0}\sigma^{(2)} = \lim_{p\to\infty}\sigma^{(2)} = 0. \qquad (66)$$

The second-approximation correction thus does not change the interpolation nature of the functional dependences on the energy derived earlier. This assertion will apparently remain valid for subsequent corrections.

The calculations of $\sigma^{(2)}$ in this study were carried out only for the ground and first excited states, for which we have $n_\xi = 0$. Expression (65) takes a simpler form in this case:

$$\sigma^{(2)}(n_\xi=0) = \left(1 - \frac{1}{2}g_{2l+1}\right)^{-1}\left[-(2l+1-m)\sum_{\nu=1}^\infty c_\nu^{(1)}\right.$$

$$+ \frac{2\varkappa+m+1}{(2l)!}\sum_{\nu=1}^\infty c_\nu^{(1)}G_\nu^{(2l+1)}$$

$$\left. + \frac{(\varkappa+1)(\varkappa+m+1)}{(2l+1)!}\sum_{\nu=1}^\infty (\nu+2l+1)c_\nu^{(1)}4pG_\nu^{(2l)}\right]. \qquad (67)$$

The functions $g_k(4p)$ and $G_k^{(\nu)}(4p)$, $k = 0, 1, 2,...$, on the right side of this expression are determined by integral relations (56) and (58). The coefficients $c_\nu^{(1)}$ in (67) can be written as follows with the help of (57) and (58):

$$c_\nu^{(1)} = -\varkappa(\varkappa+m)\frac{(4p)^{2l+1}}{\nu}\nu!U(\nu+2l+1, 2l+1, 4p),$$

$$\nu = 1, 2,... \ . \qquad (68)$$

Now using the asymptotic representation[18] of the function $U(a, b, z)$ at large values of the parameter a, we find the following estimates of the coefficients $c_\nu^{(1)}$ for large values of the index ν:

$$c_\nu^{(1)} \sim \frac{\pi^{1/2}\varkappa(\varkappa+m)(4p)^{l+3/4}}{\nu(\nu+l+1/2)^{l+3/4}}$$

$$\times\exp\left\{2p - 2\left[\left(\nu+l+\frac{1}{2}\right)4p\right]^{1/2}\right\}\left[1+O\left(\nu+l+\frac{1}{2}\right)^{-1/2}\right].$$
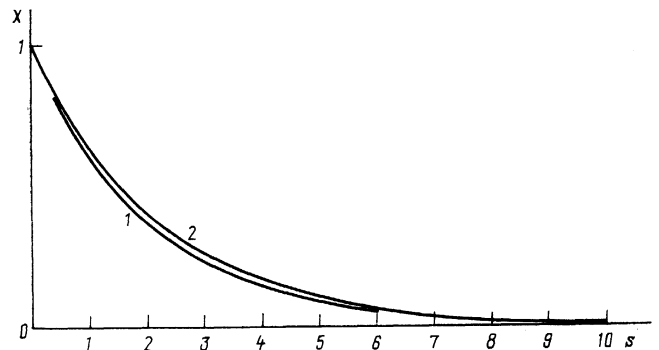$$(69)$$

FIG. 3. Wave function of the $1s\sigma_g$ ground state of the two-center system with identical unit charges at the centers as a function of the coordinate s [see (27)] (exact solution). 1—$R = 0.2$; 2—$R = 2.0$.
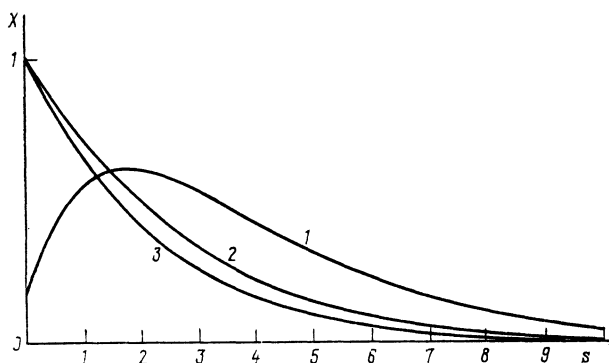
FIG. 4. The same as in Fig. 3, for the $2p\sigma_u$ state. 1—$R = 0.2$; 2—$R = 2.0$; 3—ground state, $R = 2.0$.

This behavior of $c_\nu^{(1)}$ at large values of ν causes the sums on the right side of (67) to converge for all states with $n_\xi = 0$. We have not studied the convergence of the sums in (65) in the general case.

The results calculated for the second-approximation correction to the energy with the help of (67) are shown in Figs. 1 and 2 and Table I for the $1s\sigma_g$ and $2p\sigma_u$ states.

5. DISCUSSION OF RESULTS

The most interesting results of this paper, in my opinion, are relations (45) and (46), which were derived in the first step of the iterative solution of Eqs. (37). The electron energies calculated from these formulas for the ground state, shown in Table I and Fig. 1, agree considerably better than the asymptotic expansion of Ref. 15 with the exact solution, even in the region $R < 0.5$. Over the entire range of R the deviation from the exact solution is less than 3%, as can be seen from this table. An accuracy of the same order of magnitude is achieved even in the first approximation for the $2p\pi_u$ and $2s\sigma_g$ states (Fig. 2).

Relations (45) and (46) are considerably less successful in the case of the $2p\sigma_u$ state (Fig. 2). Corresponding calculations carried out for the $2d\sigma_g$ state suggest that the accuracy of the first approximation is always considerably worse for states with a nonzero node quantum number $n_\eta = l - m$. Calculations of $X(s)$ carried out in this study on the basis of exact expressions (26) and (28), with the coeffi-

cients a_j^{nlm} from the tables of Ref. 12, show that the functional dependence $X(s)$ does not change qualitatively with R for the states with $n_\eta = 0$ (Fig. 3). For the states with $n_\eta = 1,2,...$, in contrast, the electron density is redistributed noticeably (Fig. 4). It may be that the difference between the accuracy levels of the first approximation (and, evidently, those of all subsequent approximations) for these two types of states stems from specifically this circumstance.

As can be seen from Table I and Figs. 1 and 2, the second-approximation correction improves the accuracy of the results considerably. For the ground state, the maximum deviation from the exact solution decreases to $\sim 0.5\%$. Estimates of the type in (69) can apparently be found for higher approximations also, so in principle they could be calculated. If this is the case, solution (26), (33) might be thought of as yet another representation of the exact solution of the symmetric two-center problem.

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