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Method for One Particle Bound to Two Identical Fixed Centers: Application to H_2^+

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A method is presented for the quantum-mechanical problem of one particle moving in the field of two identical fixed centers. An equation for the problem is derived in both position and momentum space as a special limiting case of our general method for the three-body problem. When applied to the H_2^+ problem, using the Coulomb-Sturmian set as an expansion basis, the method gives an infinite secular equation for the energy eigenvalues which can be solved *exactly* in the limits as the internuclear distance goes to zero and to infinity. Numerical results are also reported for the energy as a function of internuclear distance for the $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, and $2\sigma_u$ states of H_2^+.

I. INTRODUCTION

It is well known that in the H_2^+ problem with fixed nuclei the variables may be separated by using prolate spheroidal coordinates[1]; an approximate solution along those lines has been worked out.[2] It is interesting to note that even though the variables separate, an exact solution in the strictest sense of the word is not obtained by that method. This comes about because the energy eigenvalues for the problem, which depend on the distance d between the two centers, are the roots of an equation involving an infinite continued fraction.[2] The roots can be found exactly by that method for $d=0$, and a numerical solution is necessary for $d\neq 0$. The solution by Bates, Ledsham, and Stewart has come to be called "exact" because it separates the variables; we also, with the above qualification, will refer to it in that way. There have also been a number of other methods reported in the literature for H_2^+.[3,4]

The purpose of this paper is to present a general expansion method for the quantum-mechanical problem of one particle moving in the field of two identical fixed centers with minimal conditions on the pair potential. The variables need not separate for our method to be useful. In this paper, we apply it to H_2^+ as the most obvious example at hand. As a bonus, we obtain the *exact* energy eigenvalues for H_2^+ in the two limits as $d\to 0$ and as $d\to\infty$, as well as finding some new, simple, useful, approximate solutions for the energy eigenvalues and wave functions in both position and momentum space for nonzero d.

The use of Sturmian functions is central to our method. Indeed, the use of Sturmian functions in atomic and molecular physics is by no means new. Hylleraas investigated them as an expansion basis for the helium atom in 1928.[5] More recently, they have found application in e-H scattering calculations,[6] in our method for the three-body problem,[7] and in conjunction with the Faddeev equations for three-particle problems.[8] Sturmian functions have also been used to obtain lower bounds for the H_2^+ energy spectrum.[9] This approach[9] is based on the method of truncated operators, which is similar to but actually different from our treatment of the integral equation for the H_2^+ problem given in Secs. IV and V.

One may well ask, why spend time on H_2^+? One reason for doing so was to see if the H_2^+ problem with fixed nuclei was recoverable from our general treatment of the three-body problem[7,10] as a special limiting case. More importantly, the method presented here can be generalized in a relatively straightforward way to treat diatomic molecules with more than one electron. But first it must be thoroughly tested for H_2^+.

II. REVIEW OF SOME THREE-BODY RESULTS

It has been shown by Eyges[11] that for a system of three particles having the same mass and interacting through pair potentials, the wave function decomposes as a sum of three parts. For a system of three particles of *arbitrary* mass governed by a Hamiltonian of the form

$$H=\sum_{i=1}^{3}\frac{p_i^2}{2m_i}+\sum_{i<j}V_{ij}(\vec{r}_i-\vec{r}_j)\ ,$$

we have shown that the exact wave function for the problem also decomposes as a sum of three parts.[7,10] Separating out the center-of-mass motion, the wave function for bound states is

$$\Psi=\psi_{12}(\vec{r}_{12},\vec{\rho}_3)+\psi_{23}(\vec{r}_{23},\vec{\rho}_1)+\psi_{31}(\vec{r}_{31},\vec{\rho}_2),$$

where the ψ_{ij} are different functions of their arguments and the following sets of center-of-mass coordinates are used:

$$\vec{R}=(m_i\vec{r}_i+m_j\vec{r}_j+m_k\vec{r}_k)M^{-1},$$

$$\vec{r}_{ij}=\vec{r}_i-\vec{r}_j,$$

$$\vec{\rho}_k = \vec{r}_k - (m_i \vec{r}_i + m_j \vec{r}_j)\,(m_i + m_j)^{-1}\,.$$

The three sets of coordinates are generated by allowing i, j, and k to assume the values 1, 2, and 3 in cyclical permutation, and M is the total mass. The ψ_{ij} are shown to obey a coupled set of equations.[7,10]

If two of the three particles are *identical* (say, particles 1 and 3) so that the total potential for the problem is

$$V = V_{12}(\vec{r}_{12}) + V_{12}(-\vec{r}_{23}) + V_{31}(|\vec{r}_{31}|)\,,$$

we then show that there are only two independent ψ_{ij} (i. e., $\psi_{12} = \psi_{23}$) and the wave function for the problem is[7,10]

$$\Psi^{S,A} = \psi_{12}^{+,-}(\vec{r}_{12}, \vec{\rho}_3) \pm \psi_{12}^{+,-}(-\vec{r}_{23}, \vec{\rho}_1) + \psi_{31}^{e,o}(\vec{r}_{31}, \vec{\rho}_2)\,,$$

where we have either symmetric (upper sign) or antisymmetric (lower sign) solutions upon exchange of particles 1 and 3. Note that the e and o superscripts of ψ_{31} denote evenness or oddness of ψ_{31} with respect to its first argument. For bound-state solutions, ψ_{12} and ψ_{31} obey the following set of coupled equations in position space[7,10]:

$$\psi_{12}^{+,-}(\vec{r}_{12}, \vec{\rho}_3) = -\int\int d^3r'_{12}\, d^3\rho'_3\, v_{12}(\vec{r}\,'_{12}) G_0(\vec{r}_{12} - \vec{r}\,'_{12}, \vec{\rho}_3 - \vec{\rho}\,'_3)\,[\psi_{12}^{+,-}(\vec{r}\,'_{12}, \vec{\rho}\,'_3) \pm \psi_{12}^{+,-}(-\vec{r}\,'_{23}, \vec{\rho}\,'_1) + \psi_{31}^{e,o}(\vec{r}\,'_{31}, \vec{\rho}\,'_2)]\,, \tag{1a}$$

$$\psi_{31}^{e,o}(\vec{r}_{31}, \vec{\rho}_2) = -\int\int d^3r'_{31} d^3\rho'_2\, v_{31}(\vec{r}\,'_{31}) G_0(\vec{r}_{31} - \vec{r}\,'_{31}, \vec{\rho}_2 - \vec{\rho}\,'_2)\,[\psi_{12}^{+,-}(\vec{r}\,'_{12}, \vec{\rho}\,'_3) \pm \psi_{12}^{+,-}(-\vec{r}\,'_{23}, \vec{\rho}\,'_1) + \psi_{31}^{e,o}(\vec{r}\,'_{31}, \vec{\rho}\,'_2)]\,, \tag{1b}$$

where the Green's function for bound states is the solution to the following differential equation:

$$\{\tfrac{1}{2}(m/m_i + m/m_j)\nabla^2_{r_{ij}} + \tfrac{1}{2}[m/(m_i + m_j) + m/m_k]\nabla^2_{\rho_k} - K^2\}G_0 = -\delta(\vec{r}_{ij} - \vec{r}\,'_{ij})\delta(\vec{\rho}_k - \vec{\rho}\,'_k)\,,$$

and where

$$K^2 = m|E|/\hbar^2,\ \ v_{ij} = mV_{ij}/\hbar^2\,,$$

and the choice of m sets the mass scale. It is easy to show that[7]

$$\langle \vec{r}_{12}, \vec{\rho}_3 |\, G_0 \,| \vec{r}\,'_{12}, \vec{\rho}\,'_3, \rangle \equiv \langle \vec{r}_{23}, \vec{\rho}_1 |\, G_0 \,| \vec{r}\,'_{23}, \vec{\rho}\,'_1 \rangle \equiv \langle \vec{r}_{31}, \vec{\rho}_2 |\, G_0 \,| \vec{r}\,'_{31}, \vec{\rho}\,'_2 \rangle$$

and that G_0 in the frame $(\vec{r}_{12}, \vec{\rho}_3)$, for example, is given in integral form by

$$G_0(\vec{r}_{12} - \vec{r}\,'_{12}, \vec{\rho}_3 - \vec{\rho}\,'_3) = \frac{1}{(2\pi)^6}\int\int d^3k\, d^3\kappa\, \frac{\exp[i\vec{k}\cdot(\vec{r}_{12} - \vec{r}\,'_{12}) + i\vec{\kappa}\cdot(\vec{\rho}_3 - \vec{\rho}\,'_3)]}{\alpha_{12}k^2 + \beta_3\kappa^2 + K^2}\,, \tag{2}$$

where

$$\alpha_{ij} = \tfrac{1}{2}(m/m_i + m/m_j);\qquad \beta_k = \tfrac{1}{2}[m/(m_i + m_j) + m/m_k]\,.$$

III. SPECIAL CASE $v_{31} \equiv 0$ AND $m_2/m_1 \to 0$

In this section, we derive an equation for the wave function of a particle moving in the field of two identical fixed centers a distance d apart. We do this as a special case of our general formulation of the three-body problem where the Pauli principle on exchange of particles 1 and 3 has been included, and where we set v_{31} to zero and take the limit as $m_2/m_1 \to 0$. This special case represents the hydrogen molecular ion in the fixed-nuclei approximation, if we choose particles 1 and 3 as protons and particle 2 as an electron.

We see immediately that if we turn off the interaction between the two nuclei by setting v_{31} to zero, then from Eq. (1b), ψ_{31} is also zero, and for the remaining equation we have

$$\psi_{12}^{+,-}(\vec{r}_{12}, \vec{\rho}_3) = -\int\int d^3r'_{12}\, d^3\rho'_3\, v_{12}(\vec{r}\,'_{12}) \times G_0(\vec{r}_{12} - \vec{r}\,'_{12}, \vec{\rho}_3 - \vec{\rho}\,'_3) \times [\psi_{12}^{+,-}(\vec{r}\,'_{12}, \vec{\rho}\,'_3) \pm \psi_{12}^{+,-}(-\vec{r}\,'_{23}, \vec{\rho}\,'_1)]\,. \tag{3}$$

We set the mass scale by choosing $m = m_2$ and note that the mass ratio m_2/m_1 in Eq. (3) only appears in G_0 and in the second term of the total wave function under the integral sign. Taking the limit as $m_2/m_1 \to 0$, we get for G_0 as $m_2/m_1 \to 0$,

$$\lim G_0(\vec{r}_{12} - \vec{r}\,'_{12}, \vec{\rho}_3 - \vec{\rho}\,'_3) = \delta(\vec{r}_{31} - \vec{\rho}\,'_3) g_0^B(\vec{r}_{12} - \vec{r}\,'_{12})$$

where

$$g_0^B(\vec{r}_{12} - \vec{r}\,'_{12}) \equiv \frac{1}{(2\pi)^3}\int d^3k\, \frac{\exp[i\vec{k}\cdot(\vec{r}_{12} - \vec{r}\,'_{12})]}{\frac{1}{2}(k^2 + K_\beta^2)}\,.$$

Here, we have evaluated the integral on κ in

Eq. (2) explicitly, taken the limit as $m_2/m_1 \to 0$, and used the following representation for the Dirac δ function:

$$\delta(\vec{\rho}-\vec{\rho}\,')=\lim\left(\frac{\exp[-(1/\sqrt{\epsilon})\,|\vec{\rho}-\vec{\rho}\,'|\,]}{4\pi\epsilon\,|\vec{\rho}-\vec{\rho}\,'|}\right)\quad\text{as } \epsilon\to 0\ .$$

Using the relations between the three sets of center-of-mass coordinates, we also see that

$$\vec{r}\,'_{23}=-\vec{r}\,'_{12}-\vec{r}\,'_{31}\ ,$$

$$\lim\vec{\rho}\,'_3=\vec{r}\,'_{31}\qquad\text{as } m_2/m_1\to 0;$$

$$\lim\vec{\rho}\,'_1=-\vec{r}\,'_{31}\qquad\text{as } m_2/m_1\to 0\ .$$

Utilizing the above results, we obtain the equation

$$\psi_B^{+,-}(\vec{r}_{12};\vec{d})=-\int d^3r'_{12}\,v_{12}(\vec{r}\,'_{12})\,g_0^B(\vec{r}_{12}-\vec{r}\,'_{12})\times[\psi_B^{+,-}(\vec{r}\,'_{12};\vec{d})\pm\psi_B^{+,-}(\vec{r}\,'_{12}+\vec{d};-\vec{d})],\qquad(4)$$

where we have defined $\vec{r}_{31}\equiv\vec{d}$. Equation (4) is an equation in position space for a function of one vector variable and a constant vector $\vec{d}$ as a parameter. It is important to note that in setting v_{31} to zero and taking the limit as $m_2/m_1\to 0$, the problem loses much of its three-body character. Physically, we now have a situation where one particle is moving in the field of two noninteracting potentials a fixed distance apart.

We find it convenient to transform Eq. (4) into momentum space. Let us then define the following Fourier-transform pair:

$$\psi_B^{+,-}(\vec{r};\vec{d})\equiv[1/(2\pi)^{3/2}]\int d^3k\,\phi_B^{+,-}(\vec{k};\vec{d})\,e^{i\vec{k}\cdot\vec{r}}\ ,$$

$$\phi_B^{+,-}(\vec{k};\vec{d})\equiv[1/(2\pi)^{3/2}]\int d^3r\,\psi_B^{+,-}(\vec{r};\vec{d})\,e^{-i\vec{k}\cdot\vec{r}}\ .$$

Performing the Fourier transform of Eq. (4), we get

$$\phi_B^{+,-}(\vec{k};\vec{d})=-[(2\pi)^3(\tfrac{1}{2}k^2+K_B^2)]^{-1}\int\int d^3r\,d^3k'\,v_{12}(\vec{r})\times e^{i\vec{r}\cdot(\vec{k}\,'-\vec{k})}\,[\phi_B^{+,-}(\vec{k}\,';\vec{d})\pm e^{i\vec{k}\,'\cdot\vec{d}}\phi_B^{+,-}(\vec{k}\,';-\vec{d})]\ .\qquad(5)$$

Evaluating the integral over the potential gives[12]

$$\phi_B^{+,-}(\vec{k};\vec{d})=-[(2\pi)^3(\tfrac{1}{2}k^2+K_B^2)]^{-1}\int d^3k'\,w(\vec{k}\,'-\vec{k})\times[\phi_B^{+,-}(\vec{k}\,';\vec{d})\pm e^{i\vec{k}\,'\cdot\vec{d}}\phi_B^{+,-}(\vec{k}\,';-\vec{d})]\ ,\qquad(6)$$

where

$$w(\vec{y})=\int d^3r\,v_{12}(\vec{r})\,e^{i\vec{r}\cdot\vec{y}}\ .$$

The total wave function in both position and momentum space is

$$\Psi_B^{S,A}(\vec{r}_{12};\vec{d})=\psi_B^{+,-}(\vec{r}_{12};\vec{d})\pm\psi_B^{+,-}(\vec{r}_{12}+\vec{d};-\vec{d})\ ,\qquad(7)$$

$$\Phi_B^{S,A}(\vec{k}_{12};\vec{d})=\phi_B^{+,-}(\vec{k}_{12};\vec{d})\pm e^{i\vec{k}_{12}\cdot\vec{d}}\phi_B^{+,-}(\vec{k}_{12};-\vec{d})\ .\qquad(8)$$

In the equations of this section, we have used the subscript and superscript B to denote the special case of a three-body problem where $v_{31}=0$ and $m_2/m_1\to 0$. Equation (5) is the basic equation we wish to investigate.

Some comments are in order concerning Eqs. (4) and (5). The conventional treatment of the identical two-center problem is to apply the Born-Oppenheimer approximation by first writing the Schrödinger equation for the motion of the less massive particle in the field of the two identical fixed centers, imposing center-of-inversion symmetry or antisymmetry on the wave function, and then solving for the bound-state energies as a function of internuclear separation. We have adopted a different approach. We started with the three-body problem where the Pauli principle on exchange of the two identical particles (the two centers) was incorporated. We then obtained an equation in either position or momentum space for the first step in the Born-Oppenheimer approximation procedure by setting v_{31} to zero and taking the limit as $m_2/m_1\to 0$. The two approaches to the problem are equivalent.

IV. SECULAR EQUATION FOR THE σ STATES: USE OF STURMIAN FUNCTIONS

In this section, we derive the secular equation which results when $\phi_B^{+,-}(\vec{k};\vec{d})$ of Eq. (5) is expanded in an infinitely denumerable, complete set of functions in the Hilbert space L^2. We also show how the pair potential can be eliminated from the integrations. In this paper we restrict our attention to the σ states of the diatomic molecular ion, since a secular equation for the other states may easily be derived using the method presented here.

For bound states, the total wave function is an element of the Hilbert space L^2. It follows immediately that $\phi_B^{+,-}$ and $\psi_B^{+,-}$ are also elements in L^2. For σ states we may, therefore, expand $\phi_B^{+,-}$ as follows:

$$\phi_B^{+,-}(\vec{k};\vec{d})=\sum_{nl}a_{nl}^{+,-}(d)(-i)^l F_{nl}^{\beta}(k)(4\pi)^{-1}\times(2l+1)P_l(\cos\theta)\ ,\qquad(9)$$

where the phases $(-i)^l$ are introduced as a matter of convenience; the set $\{F_{nl}^{\beta}\}$ is any infinitely denumerable complete set of functions on the interval $[0,\infty)$; θ is the angle between $\vec{k}$ and $\vec{d}$, and the $a_{nl}^{+,-}(d)$ are unknown coefficients which depend implicitly on d as a parameter. Since we have set v_{31} to zero, the total potential for the problem is

$$v_t=v_{12}(\vec{r}_{12})+v_{12}(-\vec{r}_{23})\equiv Su(\vec{r}_{12})+Su(-\vec{r}_{23})\ ,\qquad(10)$$

where $u(\vec{r})$ is the shape of the potential and S is its strength. Here, v_{12} is quite general but must satisfy the same conditions imposed by Kato.[13]

The conventional way of finding a secular equation for the problem would be to substitute Eq. (9) for $\phi_B^{+,-}$ in Eq. (6), multiply through by

$$(+i)^{l'} F^{\beta}_{n'l'}(k) P_{l'}(\cos\theta) \,,$$

and integrate with respect to $\vec{k}$. This would give an integration over the Fourier transform of v_{12}. Such an integration is often undesirable for singular potentials, and how this can be avoided by using the properties of the Sturmian set[14–16] for the analogous pair problem will be shown below.

Let our pair potential be nonzero and everywhere attractive and let $S^{\alpha}_{nlm}(\vec{k})$ denote the Sturmian set for it, then[15]

$$S^{\alpha *}_{nlm}(\vec{y}) = -\left[2s\lambda_{nl}/(2\pi)^3(y^2+\alpha^2)\right] \times \int\int d^3k\, d^3r\, u(\vec{r}) S^{\alpha *}_{nlm}(\vec{k})\, e^{i\vec{r}\cdot(\vec{y}-\vec{k})} \,, \quad (11)$$

where α^2 is a positive number; the $\{\lambda_{nl}\}$ is a set of positive numbers; $u(\vec{r})$ is the shape of the pair potential; and s is its strength. It can be shown that for a given s there will be, in general, a countably infinite set of positive numbers $\{\lambda_{nl}\}$ (possibly degenerate) for some positive number α^2. If we now imagine the family of Sturmian sets generated by regarding α as a continuous variable, we see that α^2 will depend on s and $\{\lambda_{nl}\}$ through the solution of Eq. (11):

$$\alpha^2 = f(s, \{\lambda_{nl}\}) \,.$$

For most applications, the set $\{\lambda_{nl}\}$ is chosen such that its smallest member (λ_{10}) is 1.

The secular equation we propose, which eliminates the explicit integration over w, is obtained by multiplying Eq. (5) by $(\frac{1}{2}k^2+K_B^2)$, substituting Eq. (9) in (5), multiplying through by $(+i)^{l'} S^{\alpha *}_{n'l'}(k) \times P_{l'}(\cos\theta)$ and integrating with respect to $\vec{k}$, and using Eq. (11) to eliminate the explicit appearance of the pair potential. We obtain the result

$$\begin{aligned}\sum_n a^{+,-}_{nl'}\Big[\tfrac{1}{2} C^{\alpha\beta}_{n'l'nl'} &+ K_B^2 D^{\alpha\beta}_{n'l'nl'} - (S/2s\lambda_{n'l'})(C^{\alpha\beta}_{n'l'nl'} + \alpha^2 D^{\alpha\beta}_{n'l'nl'})\Big] \\ &= \pm (S/4s\lambda_{n'l'}) \int_0^\infty dk' \int_{-1}^{1} dz\, k'^2 e^{ik'dz}\Big[\sum_{nl} a^{+,-}_{nl}(i)^{l'+l} \\ &\quad\times (2l+1)(k'^2+\alpha^2) S^{\alpha}_{n'l'}(k') F^{\beta}_{nl}(k') P_{l'}(z) P_l(z)\Big] \,, \end{aligned} \quad (12)$$

where the following families of integrals have been defined:

$$C^{\alpha\beta}_{n'l'nl'} \equiv \int_0^\infty dk\, k^4 S^{\alpha}_{n'l'}(k) F^{\beta}_{nl'}(k) \,,$$

$$D^{\alpha\beta}_{n'l'nl'} \equiv \int_0^\infty dk\, k^2 S^{\alpha}_{n'l'}(k) F^{\beta}_{nl'}(k) \,.$$

In Eq. (12), the Fourier transform of the pair potential does not appear and the vector $\vec{d}$ has been chosen along the z axis. Equation (12) is the secular equation for the problem using our method, where the set $\{F^{\beta}_{nl}\}$ is arbitrary. If we so choose, we may use the Sturmian set itself as an expansion basis, set $\beta=\alpha$, and make use of the orthogonality condition in momentum space[15]:

$$\int_0^\infty dk\, k^2 S^{\alpha}_{n'l'}(k)(k^2+\alpha^2) S^{\alpha}_{nl'}(k) = s^2 \lambda_{n'l'} \delta_{n'n} \,, \quad (13)$$

to obtain

$$\begin{aligned}\sum_n a^{+,-}_{nl'}\left(\tfrac{1}{2}\Gamma^{\alpha\alpha}_{n'l'nl'} + K_B^2 \Delta^{\alpha\alpha}_{n'l'nl'} - \tfrac{1}{2}Ss\,\delta_{n'n}\right) \\ = \pm (S/4s\lambda_{n'l'}) \sum_{nl} a^{+,-}_{nl}(i)^{l'+l}(2l+1) I^{\alpha\alpha}_{n'l'nl}(d) \,. \end{aligned} \quad (14)$$

In Eq. (14), we have defined the following expressions:

$$\Gamma^{\alpha\alpha}_{n'l'nl'} \equiv \int_0^\infty dk\, k^4 S^{\alpha}_{n'l'}(k) S^{\alpha}_{nl'}(k) \,, \quad (15)$$

$$\Delta^{\alpha\alpha}_{n'l'nl'} \equiv \int_0^\infty dk\, k^2 S^{\alpha}_{n'l'}(k) S^{\alpha}_{nl'}(k) \,, \quad (16)$$

$$I^{\alpha\alpha}_{n'l'nl} \equiv \int_0^\infty \int_{-1}^{1} dk\, dz\, k^2(k^2+\alpha^2) S^{\alpha}_{n'l'}(k) S^{\alpha}_{nl}(k) \times e^{ikdz} P_{l'}(z) P_l(z) \,. \quad (17)$$

Equation (14) is the final secular equation for the σ-like states of the problem of one particle moving in the field of two fixed centers when ϕ_B is expanded in the Sturmian set for the analogous pair problem.

If we now specialize to the H_2^+-like problem, our pair potential is

$$v_{12}(\vec{r}) = Su(\vec{r}) \equiv (Ze^2 m_e/\hbar^2)(-1/r) \,,$$

and the Sturmian sets for the Coulomb pair potential in position and momentum space are[15]

$$\tilde{S}^{\alpha}_{nl}(r) = -\tilde{N}^{\alpha}_{nl} r^l e^{-\alpha r} L^{2l+1}_{n+l}(2\alpha r) \,, \quad (18)$$

$$\tilde{N}^{\alpha}_{nl} = \{\alpha(n-l-1)!/2[(n+l)!]^3\}^{1/2}(2\alpha)^{l+1} \,;$$

$$S^{\alpha}_{nl}(k) = N^{\alpha}_{nl}\left[k^l/(k^2+\alpha^2)^{l+2}\right] C^{l+1}_{n-l-1} \times \left[(k^2-\alpha^2)/(k^2+\alpha^2)\right] \,, \quad (19)$$

$$N^{\alpha}_{nl} = 2^{2(l+1)}\left[\alpha(n-l-1)!/\pi(n+l)!\right]^{1/2} nl!\,\alpha^{l+2} \,.$$

The L^p_q are the associated Laguerre polynomials, and the C^p_q are the Gegenbauer polynomials. The functional relationship between α, s, and the set of numbers $\{\lambda_{nl}\}$ is especially simple for the Coulomb potential and given by[15]

$$\alpha^2 = s^2 \,, \quad (20)$$

$$\lambda_{nl} = n \,. \quad (21)$$

Closed-form expressions for the $\Gamma^{\alpha\alpha}_{n'l'nl'}$, $\Delta^{\alpha\alpha}_{n'l'nl'}$, and $I^{\alpha\alpha}_{n'l'nl}$ may easily be found and are given in the Appendix.

The total wave functions in both position and momentum space are given by Eqs. (7) and (8), where we have the following explicit expansions for the

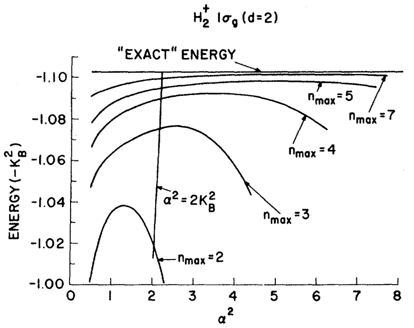

FIG. 1. Energy as a function of α^2 and the order of truncation for the $1\sigma_g$ state of H_2^+ for $d=2$. Distances and energies are all in a.u.

H_2^+ problem:

$$\psi_B^{+,-}(\vec{r};\,\vec{d})=\sum_{nl} a_{nl}^{+,-}(d)\tilde{S}_{nl}^{\alpha}(r)(4\pi)^{-1}(2l+1)\,P_l(\cos\theta)\,, \tag{22}$$

$$\phi_B^{+,-}(\vec{k};\,\vec{d})=\sum_{nl} a_{nl}^{+,-}(d)(-i)^l\,S_{nl}^{\alpha}(k)(4\pi)^{-1} \times (2l+1)\,P_l(\cos\theta)\ . \tag{23}$$

The $a_{nl}^{+,-}(d)$ and the $K_B^2(d)$ are found as implicit functions of d for each σ-like state from the secular Eq. (14).

V. CHOICE OF α AND EXACT SOLUTION FOR $d\to 0$ AND $d\to\infty$

In this section, we give a prescription for choosing the parameter α in Eq. (14). We also show that for the specific case of H_2^+, this choice of α gives, in a very transparent way, the exact eigenvalues to the infinite secular Eq. (14) in the limits as $d\to 0$ and as $d\to\infty$.

The method presented in Secs. III and IV depends on one arbitrary parameter α. All L^2 expansion methods have an inherent arbitrariness about them in that, generally, an infinite number of different sets of complete orthonormal functions can be used which will all converge in the mean to the exact eigenfunctions and eigenvalues for the problem. It is therefore important to examine, for each value of d, the dependence of the energy spectrum on α for successive orders of truncation of Eq. (14). We have done this for a few of the lower-lying negative-energy states of H_2^+ for several values of d and found that, in all cases, the energies rapidly become more and more independent of the choice of α as more terms in the expansion of the wave function are taken. A typical example is shown in Fig. 1.

From Eqs. (5) and (8), we see that the exact wave function has the form

$$\Phi_N^{S,A}(\vec{k};\,\vec{d})=\frac{f_N^{+,-}(\vec{k};\,\vec{d})}{(\frac{1}{2}k^2+K_{BN}^2)}\pm e^{+i\vec{k}\cdot\vec{d}}\,\frac{f_N^{+,-}(\vec{k};\,-\vec{d})}{(\frac{1}{2}k^2+K_{BN}^2)}\ , \tag{24}$$

where the analytic properties of $f_N^{+,-}$ are unknown and the subscript N denotes the set of negative-energy solutions. We can say from Eq. (24) and our knowledge of the asymptotic form of the wave function in position space that if we extend the k variable to the complex plane, the exact wave function must have a singularity where the energy denominator vanishes. If we now demand that our truncated wave function have this property, we obtain the condition

$$-\tfrac{1}{2}\alpha_N^2+K_{BN}^2=0. \tag{25}$$

Let's look at the implication of this choice for α in the equation for H_2^+. Using $\frac{1}{2}\alpha^2=K_\beta^2$ and Eq. (13), the secular Eq. (14) becomes

$$a_{n'l'}^{+,-}(\tfrac{1}{2}\lambda_{n'l'}\,s^2-\tfrac{1}{2}Ss)=\pm\frac{S}{4s\lambda_{n'l'}}\sum_{nl}a_{nl}^{+,-}(i)^{l'+l} \times(2l+1)I_{n'l'nl}^{\alpha\alpha}(d)\,. \tag{26}$$

For $d\to\infty$, we get from Eqs. (A8) and (A9) of the Appendix

$$\lim I_{n'l'nl}^{\alpha\alpha}(d)=0\quad\text{as}\ d\to\infty\,.$$

The secular equation for both the σ_g and the σ_u states is

$$a_{nl}^{+,-}(\tfrac{1}{2}\lambda_{nl}s^2-\tfrac{1}{2}Ss)=0\,.$$

Using the functional relationships for the Coulomb-Sturmian set given by Eqs. (20) and (21) together with our choice of $\alpha^2=2K_B^2$, and setting the determinant of the coefficients to zero, gives an infinite-order polynomial for K_B in factored form:

$$\prod_{n=1}^{\infty}[nK_B^2-(1/\sqrt{2})SK_B]=0,\quad d\to\infty\ . \tag{27}$$

The roots of the polynomial in K_B other than the trivial solutions are[17]

$$K_{Bn}(d\to\infty)=S/\sqrt{2}n \tag{28}$$

and the associated energy levels are given by

$$E_n(d\to\infty)=-\tfrac{1}{2}(m_eZ^2e^4/\hbar^2n^2)\,. \tag{29}$$

These are just the exact energy levels of the hydrogen atom for $m_e/m_p\to 0$ with the correct degeneracy on l, which is what we expect for the σ_g and σ_u states of H_2^+ when $d\to\infty$.

For $d\to 0$, we may not use Eqs. (A8) and (A9) of the Appendix, since in deriving them we made the assumption that $d\neq 0$. Instead, we see directly from Eq. (17) that

$$\lim_{d\to 0} I_{n'l'nl}^{\alpha\alpha}(d)=[2/(2l+1)]\,\delta_{l'l}\int_0^\infty dk\,k^2(k^2+\alpha^2)\,S_{n'l'}^{\alpha}(k)\,S_{nl}^{\alpha}(k)$$

Using Eq. (13), we have

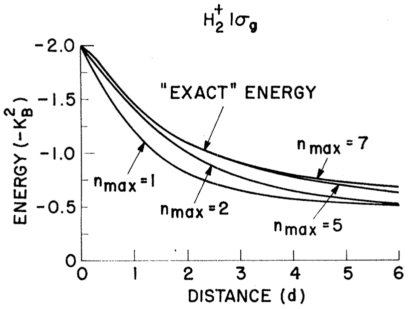

FIG. 2. Energy as a function of d and the order of truncation for the $1\sigma_g$ state of H_2^+.

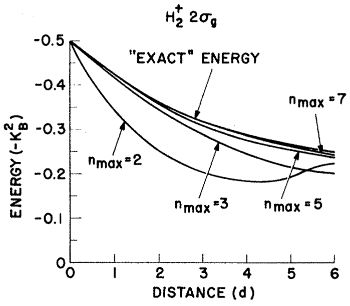

FIG. 4. Energy as a function of d and the order of truncation for the $2\sigma_g$ state of H_2^+.

$$\lim_{d\to 0} I^{\alpha\alpha}_{n'l'nl}(d) = [2/(2l+1)]\delta_{l'l} s^2 \lambda_{n'l'} \delta_{n'n} .$$

Inserting this relation in Eq. (26), we obtain

$$a^{+;-}_{n'l'}(\tfrac{1}{2}\lambda_{n'l'} s^2 - \tfrac{1}{2}Ss) = \pm \tfrac{1}{2}Ss(-1)^{l'} a^{+;-}_{n'l'} . \qquad (30)$$

For the σ_g states of H_2^+ as $d\to 0$, we obtain

$$\prod_{n=1}^{\infty} (nK_B^2 - \sqrt{2}SK_B) = 0, \qquad l \text{ even} \qquad (31)$$

$$K_{Bn}(d=0) = \sqrt{2}(S/n), \qquad l \text{ even} \qquad (32)$$

$$E_n(d=0) = -\tfrac{1}{2}(m_e 4Z^2 e^4/\hbar^2 n^2), \quad l \text{ even.} \qquad (33)$$

These are just the energy levels of a hydrogen-like atom with charge 2 for $m_e/m_p \to 0$. For l odd, there are no nontrivial σ_g roots. For σ_u states for $d\to 0$, we obtain from Eq. (30)

$$\prod_{n=1}^{\infty} (nK_B^2 - \sqrt{2}SK_B) = 0 \qquad , \quad l \text{ odd} \qquad (34)$$

$$K_{Bn}(d=0) = \sqrt{2}\,(S/n) \qquad , \quad l \text{ odd} \qquad (35)$$

$$E_n(d=0) = -\tfrac{1}{2}(m_e 4Z^2 e^4/\hbar^2 n^2), \quad l \text{ odd} \qquad (36)$$

with no nontrivial σ_u roots for even l. Again, we have the correct degeneracy on l for this limit. We see that our infinite secular Eq. (14) gives the exact results in a simple way for H_2^+ when $d\to 0$ and $d\to\infty$.

VI. COALESCENCE CONDITION FOR H_2^+

It is well known that in an n-body problem where the particles interact through Coulomb pair potentials, exact conditions on the form of the wave function may be derived in the limit as any two of the particles coalesce.[18] That is to say, if particles i and j come together, then the Coulomb singularity in the pair potential determines the form of Ψ to the first order in $|\vec{r}_i - \vec{r}_j|$. The general form for the wave function as particles i and j coalesce is known to be[18]

$$\Psi = \Psi_0[1 + Z_i Z_j \mu_{ij} r_{ij} + \vec{r}_{ij}\cdot\vec{u}_{ij} + O(r_{ij}^2)], \qquad (37)$$

where Ψ_0 is the wave function evaluated at $r_{ij}=0$; Z_i and Z_j are the charges of the particles i and j; μ_{ij} is their reduced mass, and $\vec{u}_{ij}$ is an unknown vector independent of $\vec{r}_{ij}$.

We have examined our expression for the wave function in position space given by Eqs. (7) and (22) in the limit as either particles 2 and 3 coalesce or as particles 2 and 1 coalesce, and found that it has the form of Eq. (37). For H_2^+ with $m_e/m_p \to 0$, we obtain

$$\Psi^{S,A} = \Psi_0^{S,A}[1 + g^{+,-} r_{12} + \vec{r}_{12}\cdot\vec{u}_{12} + O(r_{12}^2)], \qquad (38)$$

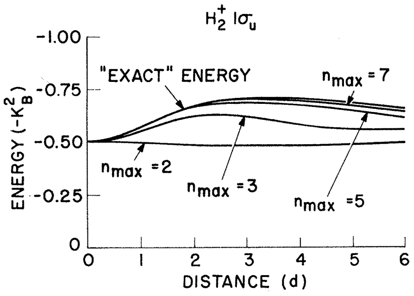

FIG. 3. Energy as a function of d and the order of truncation for the $1\sigma_u$ state of H_2^+.

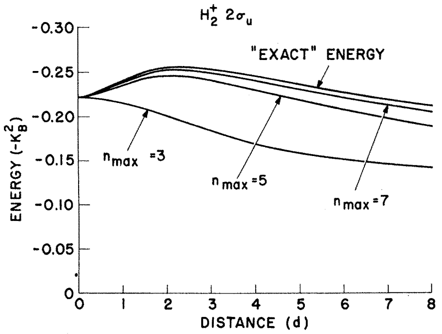

FIG. 5. Energy as a function of d and the order of truncation for the $2\sigma_u$ state of H_2^+.

TABLE I. Energies[a] and coalescence constants for $H_2^+(1\sigma_g)$ at $d=2$.

	Orders of truncation of ψ_B^+ labeled by $n_{\max}$							
	1	2	3	4	5	6	7	8
Energy[b] $(-K_B^2)$	−0.8148	−1.0182	−1.0756	−1.0886	−1.0944	−1.0974	−1.0989	−1.1000
$\Delta(-K_B^2)$	0.2878	0.0844	0.0270	0.0140	0.0082	0.0052	0.0037	0.0026
Coalescence constant[c] (g^+)	−1.1844	−0.7952	−0.9630	−1.0392	−1.0300	−0.9987	−0.9817	−0.9839
$\Delta(g^+)$	−0.1844	0.2048	0.0370	−0.0392	−0.0300	0.0013	0.0183	0.0161
α $(\alpha=\sqrt{2}K_B)$	1.2766	1.4270	1.4667	1.4756	1.4795	1.4815	1.4825	1.4832

[a] Energies are reported in a.u.

[b] "Exact" energy to five figures is −1.1026.

[c] Exact value for g^+ is −1.0.

where $g^{+,-}$ is given by

$$g^{+,-}=\left[\sum_n a_{n0}^{+,-}(4\pi)^{-1}\left(\frac{\partial}{\partial r}\tilde{S}_{n0}^{\alpha}(r)\right)_{r=0}\right](\Psi_0^{S,A})^{-1}, \quad (39)$$

$$\Psi_0^{S,A}=\sum_n a_{n0}^{+,-}(4\pi)^{-1}\tilde{S}_{n0}^{\alpha}(0)$$

$$\pm\sum_{nl}(-1)^l a_{nl}^{+,-}(4\pi)^{-1}\tilde{S}_{nl}^{\alpha}(d)(2l+1). \quad (40)$$

VII. RESULTS FOR H_2^+

We have examined all of the truncations of the secular Eq. (14) for a maximum n from 1 through 7, and the results for the energy as a function of d for the four lowest σ-states are shown and compared with the "exact" results in Figs. 2–5. For each $n_{\max}$ we kept all terms whose indices run from (1, 0) through ($n_{\max}$, $n_{\max}-1$). The total number of terms kept in the expansion of ϕ_B for a given $n_{\max}$ is

$$\text{total number}=\sum_{n=1}^{n_{\max}}, \qquad n=\tfrac{1}{2}n_{\max}(n_{\max}+1)\ .$$

In all cases examined, the energy improves as more terms in ϕ_B are included. A large number of more excited σ-states were also found which are not reported here.[19] In general, as more terms are included in the expansion, more σ states appear, and in the limit as $n_{\max}\to\infty$, we would expect to see all of them converge in the mean to the exact results. In all the calculations for each state, the value of d and order of truncation α was chosen such that

$$\tfrac{1}{2}\alpha_N^2=K_{Bn}^2\ . \quad (41)$$

For example, setting the determinant of the coefficients to zero for the first truncation ($n_{\max}=1$) of Eq. (14) for the σ_g states gives

$$K_B^2=S\alpha e^{-\alpha d}(1+\alpha d)+S\alpha-\tfrac{1}{2}\alpha^2. \quad (42)$$

Imposing Eq. (41), we get a transcendental equation for K_B in terms of d:

$$2K_B^2=S\sqrt{2}K_B e^{-\sqrt{2}K_B d}(1+\sqrt{2}K_B d)+S\sqrt{2}K_B\ . \quad (43)$$

A numerical solution yields the roots for the first truncation as a function of d shown in Fig. 2.

In Tables I and II, we give the energies and values of the coalescence constants for the $1\sigma_g$ and $1\sigma_u$ states at $d=2$ for truncations labeled by $n_{\max}$ from 1 through 8. Note the way in which the energies converge as opposed to the oscillatory way in which

TABLE II. Energies[a] and coalescence constants for $H_2^+(1\sigma_u)$ at $d=2$.

	Orders of truncation of ψ_B^- labeled by $n_{\max}$						
	2	3	4	5	6	7	8
Energy[b] $(-K_B^2)$	−0.4830	−0.6179	−0.6410	−0.6514	−0.6576	−0.6609	−0.6627
$\Delta(-K_B^2)$	0.1845	0.0496	0.0265	0.0161	0.0099	0.0066	0.0048
Coalescence constant[c] (g^-)	−0.9178	−0.8610	−0.8067	−0.8047	−0.8316	−0.8601	−0.8774
$\Delta(g^-)$	0.0822	0.1390	0.1933	0.1953	0.1684	0.1399	0.1226
α $(\alpha=\sqrt{2}K_B)$	0.9829	1.1117	1.1322	1.1414	1.1468	1.1497	1.1513

[a] Energies are reported in a.u.

[b] "Exact" energy to five figures is −0.66754.

[c] Exact value for g^- is −1.0.

TABLE III. Normalized coefficients a^{+}_{nl} for H_2^+ ($1\sigma_g$) at $d=2$.

	$(a^{+}_{nl}/4\pi)\times 10$ for orders of truncation of ψ^{+}_{B} labeled by $n_{\max}$							
	1	2	3	4	5	6	7	8
10[a]	+2.3462	+1.7984	+1.7539	+1.764 98	+1.771 65	+1.775 67	+1.778 161	+1.779 902
20		−0.3246	−0.3151	−0.302 83	−0.296 02	−0.291 90	−0.289 417	−0.287 686
21		−0.2174	−0.1831	−0.178 51	−0.176 37	−0.175 75	−0.175 276	−0.174 976
30			+0.0427	+0.035 99	+0.034 04	+0.033 89	+0.034 043	+0.034 303
31			+0.0455	+0.044 96	+0.046 22	+0.046 49	+0.046 671	+0.046 816
32			+0.0490	+0.051 44	+0.051 30	+0.051 38	+0.051 420	+0.051 407
40				+0.013 97	+0.013 11	+0.011 94	+0.011 460	+0.011 209
41				+0.008 73	+0.007 74	+0.007 90	+0.007 966	+0.008 058
42				−0.002 16	−0.001 83	−0.001 83	−0.001 786	−0.001 821
43				−0.017 18	−0.017 26	−0.017 31	−0.017 383	−0.017 409
50					−0.000 80	−0.000 73	−0.001 067	−0.001 356
51					−0.002 92	−0.003 40	−0.003 544	−0.003 570
52					−0.006 07	−0.006 18	−0.006 112	−0.006 107
53					−0.005 43	−0.005 28	−0.005 329	−0.005 343
54					+0.005 72	+0.005 73	+0.005 764	+0.005 785
60						−0.002 68	−0.002 560	−0.002 570
61						−0.002 79	−0.002 914	−0.003 075
62						−0.002 38	−0.002 532	−0.002 492
63						+0.000 16	+0.000 243	+0.000 227
64						+0.003 83	+0.003 859	+0.003 887
65						−0.001 78	−0.001 793	−0.001 805
70							−0.001 134	−0.001 087
71							−0.000 729	−0.000 720
72							+0.000 186	+0.000 080
73							+0.001 511	+0.001 528
74							+0.001 661	+0.001 698
75							−0.001 837	−0.001 860
76							+0.000 517	+0.000 522
80								+0.000 161
81								+0.000 462
82								+0.000 953
83								+0.001 151
84								+0.000 255
85								−0.001 399
86								+0.000 717
87								−0.000 140

[a] Values of $(a^{+}_{nl}/4\pi)\times 10$ are denoted in this column by the indices $(n,\ l)$.

g^{+} and g^{-} converge. The relatively poor values for g are not surprising since the coalescence condition constitutes a very severe test for any approximate wave function. Table III shows the coefficients of the normalized wave function for the $1\sigma_g$ state at $d=2$ for values of $n_{\max}$ from 1 through 8. Tables I

TABLE IV. Truncated wave function compared to "exact" wave function for H_2^+ ($1\sigma_g$), $d=2$.

Distance from center along internuclear axis[a]	Our value of the wave function in position space for orders of truncation labeled by $n_{\max}$								"Exact" value of wave function[b]
	1	2	3	4	5	6	7	8	
0.0	0.267	0.319	0.312	0.317	0.317	0.317	0.316	0.316	0.315
0.5	0.326	0.340	0.335	0.339	0.341	0.343	0.344	0.345	
1.0	0.516	0.381	0.415	0.434	0.441	0.444	0.446	0.449	0.458
1.5	0.275	0.187	0.219	0.226	0.228	0.230	0.232	0.233	
2.0	0.144	0.090	0.116	0.117	0.117	0.119	0.120	0.120	0.120
2.5	0.076	0.044	0.063	0.061	0.060	0.061	0.062	0.061	
3.0	0.040	0.021	0.034	0.030	0.031	0.032	0.031	0.030	0.030
4.0	0.011	0.005	0.010	0.007	0.008	0.008	0.007	0.007	0.007

[a] Distance given in a.u.

[b] "Exact" values taken from Ref. 2.

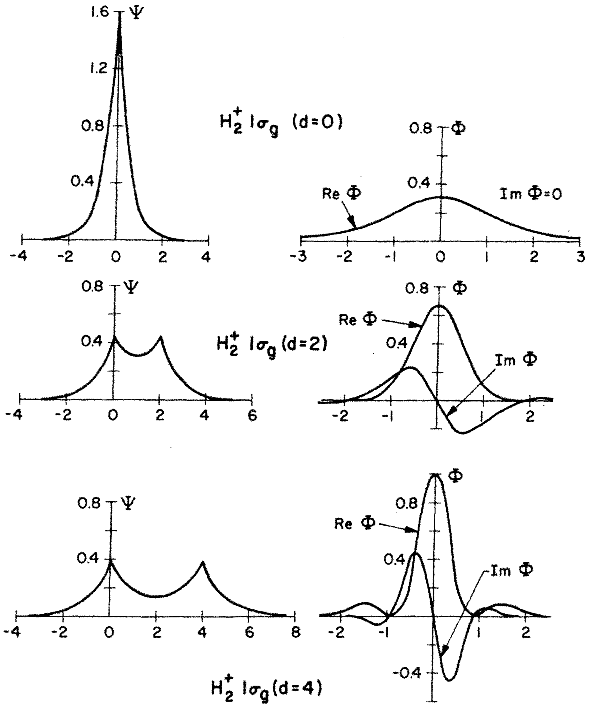

FIG. 6. Wave function for H_2^+ $(1\sigma_g)$ in position and momentum space for several values of internuclear separation (d).

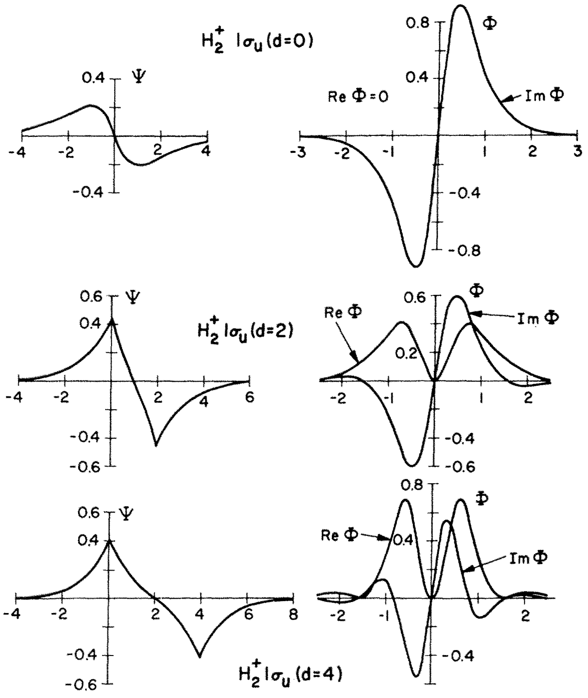

FIG. 7. Wave function for $H_2^+(1\sigma_u)$ in position and momentum space for several values of internuclear separation (d).

and III together with Eqs. (7), (8), (22), and (23) specify the wave function for the $1\sigma_g$ state with $d=2$ in both position and momentum space for various orders of approximation. Tables IV and V compare the truncated wave function to the "exact" one for the $1\sigma_g$ and $1\sigma_u$ states at $d=2$. Figures 6 and 7 show the value of the wave function along the line between the two centers in both position space and momentum space for the $1\sigma_g$ and $1\sigma_u$ states for several values of d.

VIII. DISCUSSION

We have given a new method for the problem of one particle bound to two fixed centers. We have shown how to apply this method by treating H_2^+ and obtaining the exact energy levels in the limits $d\rightarrow 0$ and $d\rightarrow\infty$, as well as some simple approximate wave functions in both momentum space and position space for $d\neq 0$.

The most immediate extension of this work is to

TABLE V. Truncated wave function compared to "exact" wave function for $H_2^+(1\sigma_u)$, $d=2$.

Distance from center along internuclear axis[a]	Our value of the wave function in position space for orders of truncation labeled by $n_{\max}$							"Exact" value of wave function[b]
	2	3	4	5	6	7	8	
0.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.5	0.161	0.169	0.187	0.193	0.197	0.200	0.202	
1.0	0.407	0.383	0.403	0.414	0.426	0.434	0.439	0.453
1.5	0.294	0.262	0.274	0.285	0.293	0.298	0.300	
2.0	0.207	0.175	0.184	0.193	0.197	0.198	0.198	0.199
2.5	0.144	0.115	0.123	0.128	0.129	0.127	0.127	
3.0	0.098	0.075	0.082	0.084	0.081	0.080	0.079	0.078
4.0	0.044	0.031	0.036	0.033	0.030	0.030	0.030	0.029

[a] Distance given in a.u.

[b] "Exact" values taken from Ref. 2.

see how large a truncation we can manage on existing computers and how good an answer we can get. We are at present attempting to streamline our calculations so that large matrix equations can be solved. We believe it is also possible to generalize the method in a straightforward way so that diatomic molecules involving two electrons can be treated. It is interesting to note from Figs. 1–5 and from Table I that we get an upper bound to each energy level of H_2^+ which improves with increasing order of truncation for all states examined including those not reported here. It is possible to show that Eq. (14) is equivalent to a linear variational calculation.[20]

ACKNOWLEDGMENTS

We acknowledge the capable efforts of Dr. R. Ring and N. Grossbard, who have done some of the analysis and all of the numerical computations for this paper.

APPENDIX: INTEGRALS $\Delta^{\alpha\alpha}_{n'l'nl'}$, $\Gamma^{\alpha\alpha}_{n'l'nl'}$, AND $I^{\alpha\alpha}_{n'l'nl}$

In this Appendix, we derive closed-form expressions for the three families of integrals defined by Eqs. (15)–(17):

$$\Delta^{\alpha\alpha}_{n'l'nl'}=N^{\alpha}_{n'l'}N^{\alpha}_{nl'}\int_0^\infty dx\,x^2Q^{\alpha}_{n'l'}(x)Q^{\alpha}_{nl'}(x),\qquad \Gamma^{\alpha\alpha}_{n'l'nl'}=N^{\alpha}_{n'l'}N^{\alpha}_{nl'}\int_0^\infty dx\,x^4Q^{\alpha}_{n'l'}(x)Q^{\alpha}_{nl'}(x)\ ,$$

where

$$Q^{\alpha}_{nl}(x)\equiv\frac{x^l}{(x^2+\alpha^2)^{l+2}}\,C^{l+1}_{n-l-1}\left(\frac{x^2-\alpha^2}{x^2+\alpha^2}\right)\ ,\qquad N^{\alpha}_{nl}\equiv2^{2(l+1)}\left[\frac{\alpha(n-l-1)!}{\pi(n+l)!}\right]^{1/2}nl!\alpha^{l+2}\ ,\tag{A1}$$

and the C^p_q are the Gegenbauer polynomials. Let

$$y=(x^2-\alpha^2)/(x^2+\alpha^2)\ ,$$

so that

$$dx=[\alpha/(1-y)^2][(1-y)/(1+y)]^{1/2}dy\ .$$

We obtain the following in terms of an integral on y:

$$\Delta^{\alpha\alpha}_{n'l'nl'}=(N^{\alpha}_{n'l'}N^{\alpha}_{nl'}/\alpha^{2l'+5}2^{2l'+4})\int_{-1}^{1}dy\,(1-y^2)^{l'+1/2}(1-y)C^{l'+1}_{n'-l'-1}(y)C^{l'+1}_{n-l'-1}(y)\ ,$$

$$\Gamma^{\alpha\alpha}_{n'l'nl'}=(N^{\alpha}_{n'l'}N^{\alpha}_{nl'}/\alpha^{2l'+3}2^{2l'+4})\int_{-1}^{1}dy\,(1-y^2)^{l'+1/2}(1+y)C^{l'+1}_{n'-l'-1}(y)C^{l'+1}_{n-l'-1}(y)\ .$$

The orthogonality relation for the Gegenbauer polynomials is[21]

$$\int_{-1}^{1}dy\,(1-y^2)^{p-1/2}C^p_q(y)C^p_r(y)=0,\qquad q\neq r\tag{A2}$$

$$\int_{-1}^{1}dy\,(1-y^2)^{p-1/2}[C^p_q(y)]^2=\{\pi2^{1-2p}(q+2p-1)!/q!(p+q)[(p-1)!]^2\}\ .\tag{A3}$$

A useful recursion formula for the C^p_q is[21]

$$2(p+q)yC^p_q(y)=(2p+q-1)C^p_{q-1}(y)+(q+1)C^p_{q+1}(y)\ .\tag{A4}$$

For all values of n' and n such that $|n'-n|>1$, we see from Eqs. (A2)–(A4) that

$$\int_{-1}^{1}dy\,(1-y^2)^{l'+1/2}(1-y)C^{l'+1}_{n'-l'-1}(y)C^{l'+1}_{n-l'-1}(y)=0\ .$$

Since a similar result holds for the Γ family of integrals, we have

$$\Delta^{\alpha\alpha}_{n'l'nl'}=\Gamma^{\alpha\alpha}_{n'l'nl'}=0,\qquad|n'-n|>1\ .\tag{A5}$$

For the case where n' and n differ by 1, we have

$$\Gamma^{\alpha\alpha}_{(n+1)l'nl'}+\alpha^2\Delta^{\alpha\alpha}_{(n+1)l'nl'}=(2N^{\alpha}_{(n+1)l'}N^{\alpha}_{nl'}/\alpha^{2l'+3}2^{2l'+4})\int_{-1}^{1}dy\,(1-y^2)^{l'+1/2}C^{l'+1}_{n-l'}(y)C^{l'+1}_{n-l'-1}(y)\ .$$

This integral is just zero by orthogonality, so we have the following result:

$$\Gamma^{\alpha\alpha}_{(n+1)l'nl'}=-\alpha^2\Delta^{\alpha\alpha}_{(n+1)l'nl'}\ .$$

The integral for $\Delta^{\alpha\alpha}_{(n+1)l'nl'}$ is

$$\Delta^{\alpha\alpha}_{(n+1)l'nl'}=(N^{\alpha}_{(n+1)l'}N^{\alpha}_{nl'}/\alpha^{2l'+5}2^{2l'+4})\int_{-1}^{1}dy\,(1-y^2)^{l'+1/2}(1-y)C^{l'+1}_{n-l'}(y)C^{l'+1}_{n-l'-1}(y)\ .$$

Using the orthogonality and the recursion relation, we obtain

$$\Delta^{\alpha\alpha}_{(n+1)l'nl'} = -\left(N^{\alpha}_{(n+1)l'}N^{\alpha}_{nl'}/\alpha^{2l'+5}2^{2l'+4}\right)\int_{-1}^{1} dy\,(1-y^2)^{l'+1/2}[(n-l')/2n][C^{l'+1}_{n-l'}(y)]^2,$$

$$\Delta^{\alpha\alpha}_{(n+1)l'nl'} = -\tfrac{1}{4}[(n-l')(n+l'+1)]^{1/2}\ .$$

Therefore, we have the result

$$\alpha^2\Delta^{\alpha\alpha}_{(n+1)l'nl'} = -\Gamma^{\alpha\alpha}_{(n+1)l'nl'} = -\tfrac{1}{4}\alpha^2[(n-l')(n+l'+1)]^{1/2}\ . \tag{A6}$$

For $n'=n$, using Eqs. (A2)–(A4), we obtain

$$\Delta^{\alpha\alpha}_{(n+1)l'nl'} = [(N^{\alpha}_{nl'})^2/\alpha^{2l'+5}2^{2l'+4}]\int_{-1}^{1} dy\,(1-y^2)^{l'+1/2}[C^{l'+1}_{n-l'-1}(y)]^2 = \tfrac{1}{2}n\ .$$

We may also show that

$$\alpha^2\Delta^{\alpha\alpha}_{nl'nl'} = \Gamma^{\alpha\alpha}_{nl'nl'}\ ,$$

therefore, we obtain

$$\alpha^2\Delta^{\alpha\alpha}_{nl'nl'} = \Gamma^{\alpha\alpha}_{nl'nl'} = \tfrac{1}{2}n\alpha^2\ . \tag{A7}$$

For the family of integrals denoted by $I^{\alpha\alpha}_{n'l'nl}(d)$, we may write from Eq. (17)

$$I^{\alpha\alpha}_{n'l'nl} = N^{\alpha}_{n'l'}N^{\alpha}_{nl}G^{\alpha\alpha}_{n'l'nl}\ ,\quad G^{\alpha\alpha}_{n'l'nl} \equiv \int_0^\infty \int_{-1}^{1} dx\,dz\,x^2(x^2+\alpha^2)Q^{\alpha}_{n'l'}(x)Q^{\alpha}_{nl}(x)P_{l'}(z)P_l(z)e^{+ixdz}\ .$$

The C^p_q which appear in the Q^{α}_{nl} are given by[21]

$$C^{l+1}_{n-l-1}(x) = \sum_{p=0}^{n-l-1} C^p_{nl}x^p.$$

Expanding each term in $Q^{\alpha}_{nl}(x)$, using the binomial theorem, we obtain

$$Q^{\alpha}_{nl}(x) = \frac{x^l}{(x^2+\alpha^2)^{n+1}}\sum_{p=0}^{n-l-1} C(n, l, \alpha, p)x^{2p}\ ,$$

where we have defined the constants $C(n, l, \alpha, p)$ as

$$C(n, l, \alpha, p) = \alpha^{2(n-l-1-p)}\sum_{p'=0}^{n-l-1} C^{p'}_{nl}\sum_{p''=0}^{p'}(-1)^{p'-p''}\binom{p'}{p''}\binom{n-l-1-p'}{p-p''}\ .$$

Substituting Eq. (A1) for the Q^{α}_{nl} and noting that the integrations and the summations may be interchanged for all n', l', n, and l gives the following:

$$G^{\alpha\alpha}_{n'l'nl} = \sum_{p'=0}^{n'-l'-1}\sum_{p=0}^{n-l-1} C(n', l', \alpha, p')C(n, l, \alpha, p)\int_0^\infty dx\int_{-1}^{1} dz\,x^2(x^2+\alpha^2)\frac{x^{l'+2p'+l+2p}}{(x^2+\alpha^2)^{n'+n+2}}P_{l'}(z)P_l(z)e^{+ixdz}\ .$$

First, consider the case when $l+l'$ is even. Then we have

$$\int_{-1}^{1} dz\,P_{l'}(z)P_l(z)e^{+ixdz} = 2\int_0^1 dz\,P_{l'}(z)P_l(z)\cos(xdz).$$

Let us also write for the P_l

$$P_l(z) = \sum_{p=0}^{l} C(l, p)z^p\ .$$

Substituting for the P_l gives

$$G^{\alpha\alpha}_{n'l'nl} = 2\sum_{p'=0}^{n'-l'-1}\sum_{p=0}^{n-l-1}\sum_{q'=0}^{l'}\sum_{q=0}^{l} C(n', l', \alpha, p')C(n, l, \alpha, p)C(l', q')C(l, q)\int_0^\infty dx\int_0^1 dz\,\frac{(x^2)^{p'+p+1+(l'+l)/2}}{(x^2+\alpha^2)^{n'+n+1}}\cos(xdz)z^{q'+q}\ .$$

Writing $(x^2)^t = (x^2+\alpha^2-\alpha^2)^t$ and expanding this expression by the binomial theorem gives

$$G^{\alpha\alpha}_{n'l'nl} = 2\sum_{p'=0}^{n'-l'-1}\sum_{p=0}^{n-l-1}\sum_{q'=0}^{l'}\sum_{q=0}^{l}\sum_{r=0}^{t} C(n', l', \alpha, p')C(n, l, \alpha, p)$$

$$\times C(l', q')C(l, q)(-1)^r\alpha^{2r}\binom{t}{r}\int_0^\infty dx\int_0^1 dz\,\frac{\cos(xdz)z^{q'+q}}{(x^2+\alpha^2)^{n'+n+1-t+r}}\ ,$$

where $t=p'+p+1+\frac{1}{2}(l'+l)$. Remember the following formula:

$$\int_0^\infty \frac{\cos(xdz)}{(x^2+\alpha^2)^m}\,dx=\frac{\pi(dz)^{m-1}e^{-\alpha dz}}{(m-1)!(2\alpha)^m}\sum_{s=0}^{m-1}\frac{(m+s-1)!}{s!(m-s-1)!}(2\alpha dz)^{-s}\quad .$$

Inserting this for the integral on x, we note that the resulting integral on z may also be done and for $d\neq 0$ has the form

$$\int_0^1 dz\, z^w e^{-\alpha dz}=-e^{-\alpha d}\sum_{u=1}^{w}\frac{w!}{(\alpha d)^u(w+1-u)!}+w!\,\frac{(1-e^{-\alpha d})}{(\alpha d)^{w+1}}\quad .$$

The final result for $I^{\alpha\alpha}_{n'l'nl}$ with $l+l'$ even and $d\neq 0$ is

$$\begin{aligned}I^{\alpha\alpha}_{n'l'nl}={}&\frac{2\pi N^{\alpha}_{n'l'}N^{\alpha}_{nl}}{\alpha^{3+l'+l}}\sum_{p'=0}^{n'-l'-1}\sum_{p=0}^{n-l-1}\sum_{q'=0}^{l'}\sum_{q=0}^{l}C(n',l',\alpha,p')C(n,l,\alpha,p)\\&\times(\alpha^2)^{-n-n'+l+l'+2+p+p'}C(l',q')C(l,q)\sum_{r=0}^{t}\sum_{s=0}^{m-1}(-1)^r\binom{t}{r}\\&\times\frac{(m+s-1)!}{(m-1)!2^{m+s}s!(m-s-1)!}\left(-e^{-\alpha d}\sum_{u=1}^{w}\frac{w!}{(w+1-u)!}(\alpha d)^{m-s-u-1}+w!\,\frac{(1-e^{-\alpha d})}{(\alpha d)^{q'+q+1}}\right)\quad .\end{aligned}\tag{A8}$$

Here, we have defined the following expressions:

$$m\equiv n'+n-p'-p-\tfrac{1}{2}(l'+l)+r,\qquad w\equiv n'+n-p'-p-\tfrac{1}{2}(l'+l)+q'+q+r-s-1\quad .$$

The family of integrals $I^{\alpha\alpha}_{n'l'nl}$ for $l'+l$ odd and $d\neq 0$ may be done in a similar fashion. The answer is

$$\begin{aligned}I^{\alpha\alpha}_{n'l'nl}={}&\frac{2\pi i N^{\alpha}_{n'l'}N^{\alpha}_{nl}}{\alpha^{3+l'+l}}\sum_{p'=0}^{n'-l'-1}\sum_{p=0}^{n-l-1}\sum_{q'=0}^{l'}\sum_{q=0}^{l}C(n',l',\alpha,p')C(n,l,\alpha,p)\\&\times(\alpha^2)^{-n-n'+l+l'+2+p+p'}\,C(l',q')C(l,q)\sum_{r=0}^{t'}\sum_{s=0}^{m'-1}(-1)^r\binom{t'}{r}\\&\times\frac{(m'+s-1)!}{m'!2^{m'+s+1}s!(m'-s-1)!}\left(-e^{-\alpha d}\sum_{u=1}^{w'}\frac{w'!}{(w'+1-u)!}(\alpha d)^{m'-s-u}+w'!\,\frac{(1-e^{-\alpha d})}{(\alpha d)^{q'+q+1}}\right)\quad ,\end{aligned}\tag{A9}$$

where the following quantities have been defined:

$$t'\equiv p'+p+1+\tfrac{1}{2}(l'+l-1),\qquad m'=n'+n-p'-p-\tfrac{1}{2}(l'+l-1)+r-1,$$

$$w'=n'+n-p'-p-\tfrac{1}{2}(l'+l-1)+q'+q+r-s-1\quad .$$

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[15] For a brief discussion of the Sturmian set and in particular the Coulomb-Sturmian set, see the Appendix of Ref. 7.

[16] See also Ref. 6 and the Appendix of L. Eyges and J. R. Jasperse, J. Math. Phys. 9, 805 (1968).

[17] This simple relationship for the roots as $d\to\infty$ occurs because of the special properties of the Coulomb pair potential. For pair potentials with more complicated functional relationships between s, α^2, and $\{\lambda_{nl}\}$, we would not get such a simple result and could, for example, obtain a finite number of roots.

[18] R. T. Pack and W. Byers Brown, J. Chem. Phys. 45, 556 (1966).

[19] It seems unnecessary to report complete information on these states here. If anyone is interested in the details, he may contact the author.

[20] In operator form, Eq. (14) is equivalent to the variational calculation

$$\frac{\partial}{\partial a^{+,-*}_{n'l'}}\{\psi^{+,-},\ (T+K_B^2)\,\psi^{+,-}+V_{12}\Psi^{S,A}\}=0\,,$$

where T is the kinetic-energy operator. The natural linear variational equations, however, involve the total wave function

$$\frac{\partial}{\partial a^{+,-*}_{n'l'}}\{\Psi^{S,A},\ (T+K_B^2)\Psi^{S,A}+(V_{12}+V_{23})\,\Psi^{S,A}\}=0\,.$$

We may show the variational equivalence of these two sets of equations by first substituting $(1\pm O)\,\psi^{+,-}$ for $\Psi^{S,A}$, where O is the operator which exchanges particles 1 and 3, by noting that $(1\pm O)\,V_{12}\Psi^{S,A}=(V_{12}+V_{23})\,\Psi^{S,A}$, and by using the transformation which relates an integral about one center of the molecule to that about the other.

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Mean Lives of Some 3*p* Levels of Neon II†

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The mean lives of six 3*p* levels of singly ionized neon have been measured using the ionic beam method with a gas target. Relative line intensities in two of the strongest multiplets have also been measured. It was found that the levels were populated according to the weight $2J+1$, where J is the quantum number for the total electronic angular momentum. The levels and the measured lifetimes in nanoseconds are $3p\,{}^4D^\circ_{7/2}$ (7.8 ± 0.5), ${}^4D^\circ_{5/2}$ (7.6 ± 0.1), ${}^4P^\circ_{5/2}$ (10.1 ± 0.4), ${}^4P^\circ_{3/2}$ (10.6 ± 0.4), ${}^2D^\circ_{3/2}$ (8.43 ± 0.07), and $3p'\,{}^2F^\circ_{7/2}$ (8.5 ± 0.3). The indicated uncertainties are the standard deviations from the means; however, an additional uncertainty of approximately 10% should be added to each value in order to account for possible systematic errors. The reported lifetimes were obtained by fitting appropriate line intensities with the sum of two exponentials and a constant. Such fits adequately described the decay of the level populations of the fast Ne^+ ions downstream from the exit aperture of the differentially pumped collision cell.

INTRODUCTION

The Atomic and Molecular Collisions Laboratory at Louisiana State University has been engaged in the study of some of the atomic and ionic multiplets of astrophysical interest which have been tabulated by Moore.[1] In this paper we report the measurement of the mean radiative lifetimes of some 3*p* levels of Ne II. A preliminary report[2] was made on some of these measurements earlier. Since that report we have made additional measurements and have modified somewhat our method of analysis.

The lifetimes were obtained using the ionic beam technique.[3-7] The apparatus and the experimental method used have been described in detail in an earlier paper.[5] Some modifications in both have been made, but the general characteristics are unchanged. Ne^+ ions were accelerated to energies between 20 and 30 keV, were magnetically analyzed after acceleration, and were directed through a differentially pumped collision cell. Helium was used for a target gas at pressures of around 10 to 40 mTorr. The decay of the electronic levels which were excited in the collision cell during collisions with the target gas was observed optically after the ions emerged into a high-vacuum observation chamber equipped with a fused-quartz window.

Radiation from the beam at a distance x downstream from the exit aperture was collected by a fused-quartz lens and focused onto the entrance slit of a Jarrell-Ash model No. 82-000 half-meter scanning monochromator equipped with an EMI 6256QB photomultiplier. The intensities of preselected lines were measured as functions of x. The beam ions were collected in a deep cup insulated from the observation chamber, and the resulting current was monitored with a Keithley model No. 410 micro-microammeter and recorded by a Keithley Model No. 370 strip-chart recorder.

I. SOLUTION OF RATE EQUATIONS

The rate equation[8] approximately describing the process of excitation of the Ne^+ levels in the collision chamber is given by