

Singly and doubly excited states of the D -dimensional helium atom

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Large-order dimensional perturbation theory (DPT) has been used to study the ground and a number of excited states of two-electron atoms for the case $L=0$. Here we present an application of recent work generalizing DPT to any higher angular-momentum state. In this work we begin the investigation of P^o states, presenting results for the energies of some of the lowest-lying states and discuss the analytic structure of these energies as functions of $1/D$. We also obtain energies of corresponding D^o states with almost no additional effort by making use of interdimensional degeneracies with the P^o states. [S1050-2947(98)06512-3]

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I. INTRODUCTION

Dimensional perturbation theory (DPT) offers an interesting alternative to conventional large-scale diagonalization of quantum Hamiltonians. Built on a perturbation formalism that uses the dimension of space as the perturbation parameter, DPT treats the kinetic energy as a perturbation dropping all derivative terms at zeroth order while including all effective potential terms at least approximately at this order. This offers a different vantage point from which to analyze the underlying dynamics of physical interactions. In particular, unlike Hartree-Fock based calculations, correlation effects are included at the lowest order ($D \rightarrow \infty$) due to the inclusion of zeroth-order contributions from all terms in the effective potential that govern the electron-electron interaction. The first-order equation brings in harmonic (i.e., molecularlike) motion, which is described naturally by the first-order perturbation equation, which is a harmonic oscillator equation. This equation also provides a set of approximate quantum numbers and a set of basis functions that reflect the correlation effects included through first order. These basis functions can thus respond automatically to a change in an external parameter (as in the case of an atom in a magnetic field) or to an internal parameter such as the nuclear charge. In atomic and molecular physics, DPT has been applied to a large number of phenomena including the atomic Zeeman [1,2] and Stark [3–5] effects, the hydrogen atom in parallel electric and magnetic fields [6,7], two-electron and many-electron atoms, ions, and molecules [3,8], van der Waals coefficients [9], atomic clusters [10,11], quasistationary states [4,6,12], density functional theory [13,14], potential scattering problems [5,15], the computation of the rotational spectra of molecules [16], and virial coefficients [17].

The derivation of tractable perturbation equations requires an expansion of the wave function in which the rotational degrees of freedom, which multiply with increasing D , are isolated within known basis functions so that perturbation equations purely in terms of internal coordinates may be derived for the unknown expansion coefficients. For S -wave states this is fairly simple [3,18,19]; thus, to date, DPT studies have focused for the most part on S^e states and their *interdimensionally degenerate* P^e counterparts (see Sec. II C).

During the past three years we have published a series of four papers [20–23], which detail the extension of the DPT

formalism to higher angular momentum states for multielectron atoms. This work completes and generalizes earlier work by Schwartz [24] and others [25] who worked solely in three dimensions. References [20] and [21] describe in detail the derivation of a finite expansion for the D -dimensional N -electron wave function using D -dimensional rotational invariance implemented through the group-theoretic method of irreducible tensors. The resulting wave-function expansion leaves the expansion coefficients dependent only on a finite number of internal coordinates. In Ref. [22] the application of the Hamiltonian to this wave-function expansion for the atomic two-electron system results in a tractable set of differential equations that allow continuation in the dimension D , i.e., allow a perturbation theory that uses D as its parameter. These differential equations also clearly reveal the complete set of exact interdimensional degeneracies for the two-electron system generalizing the work of Herrick and Stillinger [26,27], Herschbach and co-workers [28–30], and Goodson *et al.* [31], who identified some particular interdimensional degeneracies. In Ref. [23] these differential equations are solved in the large-dimension limit and a zeroth-order solution is obtained about which a perturbation series can be developed. This enables the methods of DPT to be extended to all higher angular momentum states of two-electron systems. (For a different treatment of higher angular momentum DPT as applied to molecules see Ref. [16].)

The present paper is an application of this extensive formalism. For our initial system we have chosen to study a two-electron system, specifically the $1s2p^1P^o$ and $1s2p^3P^o$ states of the helium atom. These are the lowest states of P^o symmetry in an atom that presents probably the most studied three-body problem in atomic physics. We begin in the next section by summarizing the results and procedures outlined in Refs. [22,23]. Having obtained a suitable zeroth-order approximation, we then outline the procedure for solving the perturbation equations to any order. Finally, we present the results for the $1s2p^1P^o$ and $1s2p^3P^o$ states of the helium atom and their interdimensionally degenerate counterparts the $2p3d^3D^o$ [${}_n(K,T)_N^A = {}_2(0,1)_3^0$] and $2p3d^1D^o$ [${}_n(K,T)_N^A = {}_2(0,1)_3^0$] states, respectively.

II. TWO-ELECTRON HAMILTONIAN AND LARGE- D LIMIT

The two-electron Hamiltonian in D dimensions for arbitrary angular momentum is derived in Ref. [22] by special-

izing the wave function expansion of Refs. [20,21] to a two-electron system. Reference [23] then discusses the large D limit of the Hamiltonian. Here we present a summary of the results of Refs. [22,23] and discuss the application of the equations to the calculation of the $^{1,3}P^o$ states that are the focus of this paper.

A. The Schrödinger equation

The generalized Schwartz expansion of two-electron atoms in D dimensions was developed in Ref. [22] and is given by

$$\Psi^{L,\pi}(\mathbf{r}_1, \mathbf{r}_2) = [h_{L,\pi}(\mathbf{r}_1, \mathbf{r}_2)]^T F^{L,\pi}(r_1, r_2, r_{12}), \quad (1)$$

where L is the angular momentum and π is the parity. $[h_{L,\pi}(\mathbf{r}_1, \mathbf{r}_2)]^T$ is the transpose of the column vector $h_{L,\pi}(\mathbf{r}_1, \mathbf{r}_2)$ of basis functions and $F^{L,\pi}(r_1, r_2, r_{12})$ is the column vector of expansion coefficients. The scalar quantities r_1 and r_2 are the electron-nucleus distances, while r_{12} is the interelectron separation.

If we introduce the wave-function expansion of Eq. (1) into the Schrödinger equation

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \Psi^{L,\pi}(\mathbf{r}_1, \mathbf{r}_2) = E \Psi^{L,\pi}(\mathbf{r}_1, \mathbf{r}_2), \quad (2)$$

we obtain a system of coupled differential equations

$$\mathbf{H}'_{L,\pi} F^{L,\pi} = E_{L,\pi} F^{L,\pi}, \quad (3)$$

where the matrix differential operator $\mathbf{H}'_{L,\pi}$ is

$$\begin{aligned} \mathbf{H}'_{L,\pi}(r_1, r_2, r_{12}) &= \left(-\frac{1}{2} \frac{\partial^2}{\partial r_1^2} - \frac{1}{2} \frac{\partial^2}{\partial r_2^2} - \frac{\partial^2}{\partial r_{12}^2} - \frac{r_{12}^2 + r_1^2 - r_2^2}{2r_1 r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}} \right. \\ &\quad \left. - \frac{r_{12}^2 + r_2^2 - r_1^2}{2r_2 r_{12}} \frac{\partial^2}{\partial r_2 \partial r_{12}} - \frac{Z}{r_1} - \frac{Z}{r_2} - \frac{1}{r_{12}} \right) \mathbf{I}_x \\ &\quad - \frac{(D-1+L+\gamma_2)\mathbf{I}_x + \mathbf{L}_x}{2r_1} \frac{\partial}{\partial r_1} \\ &\quad - \frac{(D-1+L+\gamma_2)\mathbf{I}_x + \mathbf{L}_x}{2r_2} \frac{\partial}{\partial r_2} \\ &\quad - \frac{(D-1+L+\gamma_2)\mathbf{I}_x + \mathbf{S}_x}{2r_{12}} \frac{\partial}{\partial r_{12}}, \end{aligned} \quad (4)$$

with $x = L - \gamma_2$ and $\gamma_2 = \left\{ \frac{1}{2} [\pi + (-1)^{L+1}] \right\}^2$, which yields $\gamma_2 = 0$ for states with $\pi = (-1)^L$ and $\gamma_2 = 1$ for states with $\pi = (-1)^{L+1}$ [32]. \mathbf{I}_x is an $[(x+1) \times (x+1)]$ -dimensional unit matrix and \mathbf{L}_x and \mathbf{S}_x are $[(x+1) \times (x+1)]$ -dimensional matrices given by

$$\mathbf{L}_x = \begin{pmatrix} x & 0 & 0 & \cdots & 0 & 0 \\ 0 & x-2 & 0 & \cdots & 0 & 0 \\ 0 & 0 & x-4 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & -(x-2) & 0 \\ 0 & 0 & 0 & \cdots & 0 & -x \end{pmatrix} \quad (5)$$

and

$$\mathbf{S}_x = \begin{pmatrix} 0 & 1 & 0 & \cdots & 0 & 0 \\ x & 0 & 2 & \cdots & 0 & 0 \\ \vdots & \ddots & \ddots & \ddots & \vdots & \vdots \\ \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & 0 & \cdots & 2 & 0 & x \\ 0 & 0 & \cdots & 0 & 1 & 0 \end{pmatrix}. \quad (6)$$

B. The Pauli principle

The system we are modeling consists of two identical fermions. Therefore, the complete wave function must be totally antisymmetric under the interchange of the two electrons. For a singlet state the spatial wave function must be symmetric, while for the triplet state it must be antisymmetric. It has been shown that this antisymmetry is ensured when the column vector $F^{L,\pi}$ satisfies the constraint (see Ref. [22])

$$F^{L,\pi}(r_1, r_2, r_{12}) = (-1)^{S+\gamma_2} N_x F^{L,\pi}(r_2, r_1, r_{12}), \quad (7)$$

where S is the total spin and the $[(x+1) \times (x+1)]$ -dimensional matrix N_x is

$$N_x = \begin{pmatrix} 0 & 0 & \cdots & 0 & 1 \\ 0 & 0 & \cdots & 1 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 1 & \cdots & 0 & 0 \\ 1 & 0 & \cdots & 0 & 0 \end{pmatrix}. \quad (8)$$

C. Interdimensional degeneracies

Equations (3) and (7) show the complete spectrum of exact interdimensional degeneracies between the $\pi = (-1)^L$ and $\pi = (-1)^{L+1}$ states. The differential equations are invariant under the replacement

$$L + \gamma_2; \pi = (-1)^L; (2S+1) = 3, 1; D \Leftrightarrow$$

$$L + \gamma_2 + 2; \pi = (-1)^{L+1}; (2S+1) = 1, 3; D - 2. \quad (9)$$

For instance, the $^{3,1}P^o$ states calculated at $D=5$ give the $^{1,3}D^o$ states at $D=3$.

D. The large-dimension limit

The goal in this section is to transform the Schrödinger equation to obtain an exact solution in the $D \rightarrow \infty$ limit. To

this end we begin by regularizing the large- Z limit with the transformations $r_i \rightarrow r_i/Z$ and $E \rightarrow Z^2 E$ and we define $\lambda = 1/Z$.

Next we transform from the variables $\{r_1, r_2, r_{12}\}$ to $\{r_1, r_2, \theta\}$, where θ is the angle subtended by the two electrons at the nucleus. This transformation eliminates the derivative cross terms in the Hamiltonian $\mathbf{H}'_{L,\pi}$.

Finally, we rewrite Eq. (3) as

$$\mathbf{H}_{L,\pi}(r_1, r_2, \theta) \Phi^{L,\pi}(r_1, r_2, \theta) = E \Phi^{L,\pi}(r_1, r_2, \theta), \quad (10)$$

with

$$\mathbf{H}_{L,\pi}(r_1, r_2, \theta) = \tilde{\mathbf{J}}^{1/2} \mathbf{H}'_{L,\pi} \tilde{\mathbf{J}}^{-1/2}, \quad (11)$$

$$\Phi^{L,\pi} = \tilde{\mathbf{J}}^{1/2} F^{L,\pi}, \quad (12)$$

$$\begin{aligned} \tilde{\mathbf{J}} &= r_1^{[(L+\gamma_2)I_x + L_x]} r_2^{[(L+\gamma_2)I_x - L_x]} \sin^{(L+\gamma_2)} \theta J, \\ J &= r_1^{(D-1)} r_2^{(D-1)} \sin^{(D-2)} \theta, \end{aligned} \quad (13)$$

where J is the Jacobian. The matrix differential operator $\mathbf{H}_{L,\pi}$ becomes

$$\mathbf{H}_{L,\pi}(r_1, r_2, \theta) = \mathbf{T} + \frac{1}{\delta^2} \mathbf{U} + V \mathbf{I}_x + \frac{1}{\delta} \mathbf{W}, \quad (14)$$

where $\delta = 1/(D+L+\gamma_2)$.

Every term in Eq. (14) is a function of $\{r_1, r_2, \theta\}$. The terms \mathbf{T} , \mathbf{U} , and $V \mathbf{I}_x$ contain the matrices \mathbf{I} and/or \mathbf{L} and hence are diagonal matrix operators. The term \mathbf{W} is a tridiagonal matrix operator with zero diagonal. Furthermore, all the terms except V are δ dependent. The terms \mathbf{T} and \mathbf{W} are kinetic terms (i.e., contain derivatives), while V is the Coulomb potential term and \mathbf{U} is an additional ‘‘potential’’ term with factors of $1/r_i^2$.

Finally, to investigate the large-dimension limit we scale the coordinates and energy as

$$\tilde{r}_i = \delta^2 r_i, \quad \tilde{E} = \frac{E}{\delta^2} \quad (15)$$

and introduce these into Eq. (10) to obtain

$$\begin{aligned} &[\delta \{ \delta \mathbf{T}(\tilde{r}_1, \tilde{r}_2, \theta) + \mathbf{W}(\tilde{r}_1, \tilde{r}_2, \theta) \} + \mathbf{U}(\tilde{r}_1, \tilde{r}_2, \theta) \\ &+ V(\tilde{r}_1, \tilde{r}_2, \theta) \mathbf{I}_x] \Phi^{L,\pi} = \tilde{E} \Phi^{L,\pi}. \end{aligned} \quad (16)$$

Notice that as $\delta \rightarrow 0$ ($D \rightarrow \infty$) the derivative terms disappear and so the electrons are stationary at the minimum of the effective potential given by $U_0(\tilde{r}_1, \tilde{r}_2, \theta) + V(\tilde{r}_1, \tilde{r}_2, \theta) \mathbf{I}_x$, where $U_0(\tilde{r}_1, \tilde{r}_2, \theta)$, a multiple of the unit matrix, is the $\delta \rightarrow 0$ limit of $\mathbf{U}(\tilde{r}_1, \tilde{r}_2, \theta)$. At the minimum of this potential the values of \tilde{r}_1, \tilde{r}_2 , and θ become $\tilde{r}_1 = r_m$, $\tilde{r}_2 = r_m$, and $\theta = \theta_m$. This ‘‘frozen’’ structure is called the *Lewis structure*. Notice that this Lewis structure is independent of angular momentum since the large- D potential contains only the matrix \mathbf{I} and not the matrices \mathbf{L} or \mathbf{S} whose elements change as angular momentum is changed.

Furthermore, the term V , containing all of the electron correlation, has no overall factor of δ and hence has a contribution at zeroth order. In other words, electron correlation effects are included at the lowest order of DPT unlike other perturbation methods that include electron correlation only at higher orders.

The values of r_m and θ_m are given by

$$c_m = \cos \theta_m = -2\bar{\lambda}[(1+\bar{\lambda}^2)^{1/2} + \bar{\lambda}] \quad (17)$$

and

$$r_m = \frac{1}{4}(1+c_m)^{-2}, \quad \bar{\lambda} = \frac{\sqrt{2}\lambda}{16}, \quad (18)$$

while the eigenvalue spectrum of \tilde{E} collapses onto a single value ϵ_0 given by

$$\epsilon_0 = -4 \frac{(1+c_m)^3}{(1-c_m)} = -\frac{1}{4r_m^2 s_m^2}, \quad (19)$$

where $s_m = \sin \theta_m$ and we will also use the notation $t_m = \tan \theta_m$. Again note that the results of the large- D limit [Eqs. (17)–(19)] hold for *any* value of the total orbital angular momentum.

E. Langmuir vibrations

The next step in developing a perturbation expansion of the Schrödinger equation is to allow for small oscillations, called Langmuir vibrations, about the Lewis structure positions. To investigate these oscillations and obtain a zeroth-order solution to the wave function we introduce the dimensionally scaled displacement coordinates x_1 , x_2 , and y through the transformations

$$\begin{aligned} \tilde{r}_1 &= r_m + \delta^{1/2} x_1, \quad \tilde{r}_2 = r_m + \delta^{1/2} x_2, \\ \theta &= \theta_m + \delta^{1/2} \frac{\sqrt{2}}{r_m} y. \end{aligned} \quad (20)$$

The displacement coordinates are substituted into $\delta^2 \mathbf{T}(\tilde{r}_1, \tilde{r}_2, \theta)$, $\delta \mathbf{W}(\tilde{r}_1, \tilde{r}_2, \theta)$, $\mathbf{U}(\tilde{r}_1, \tilde{r}_2, \theta)$, $V(\tilde{r}_1, \tilde{r}_2, \theta)$, and $\Phi^{L,\pi}(\tilde{r}_1, \tilde{r}_2, \theta)$, which are then expanded in powers of $\delta^{1/2}$, while \tilde{E} is expressed as a power series in δ . These expansions are then substituted into Eq. (16) and by equating coefficients of $\delta^{1/2}$ we obtain a set of equations for ϵ_i and $\Phi_i^{L,\pi}$.

The coefficients of δ^0 give the large- D energy ϵ_0 as derived above, but we get no information about Φ_0 . The coefficient of $\delta^{1/2}$ in the Hamiltonian is zero since this coefficient is a first derivative with respect to $\delta^{1/2}$ evaluated at $\delta=0$, which is at the minimum of the potential. Thus the $\delta^{1/2}$ terms give us no information about Φ_1 . Finally, the coefficient of δ , i.e., second order in $\delta^{1/2}$, gives us a coupled differential equation for ϵ_1 and Φ_0 . Specifically,

$$\begin{aligned} &[\mathbf{T}_2(x_1, x_2, y) + \mathbf{U}_2(x_1, x_2, y) + V_2(x_1, x_2, y) \mathbf{I}_x \\ &+ \mathbf{W}_2] \Phi_0^{L,\pi}(x_1, x_2, y) = \epsilon_1 \Phi_0^{L,\pi}(x_1, x_2, y), \end{aligned} \quad (21)$$

where T_2 and U_2 multiply the unit matrix I_x and W_2 multiplies the nondiagonal matrix S_x and is independent of the displacement coordinates. So the term W_2 serves to couple the $x+1$ differential equations in Eq. (21).

Equation (21) is invariant under the substitution $x_1 \leftrightarrow x_2$, so if we transform to symmetry coordinates

$$q_1 = \frac{1}{\sqrt{2}}(x_1 - x_2), \quad x = \frac{1}{\sqrt{2}}(x_1 + x_2) \quad (22)$$

the variable q_1 separates from the other variables and we are left with x and y still coupled. The δ -order Hamiltonian becomes

$$\left[-\frac{1}{2} \left(\frac{\partial^2}{\partial q_1^2} + \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + ux^2 + vxy + wy^2 + \frac{1}{2} \omega_1^2 q_1^2 - \frac{3}{2r_m^2 s_m^2} \right] I_x - \frac{S_x}{2r_m^2 s_m t_m}, \quad (23)$$

where u , v , and w are functions of r_m , θ_m , and λ and

$$\omega_1^2 = \frac{2}{r_m^3} \left[\frac{3}{8r_m s_m^2} - 1 - \frac{\lambda(1+c_m)}{2[2(1-c_m)]^{3/2}} \right]. \quad (24)$$

We can then separate x and y by transforming to normal coordinates using the transformation

$$\begin{pmatrix} q_2 \\ q_3 \end{pmatrix} = \begin{pmatrix} -\sin \chi & \cos \chi \\ \cos \chi & \sin \chi \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}, \quad (25)$$

where χ is given by

$$\tan \chi = \frac{(w-u) \left[1 + \sqrt{1 + \left(\frac{2v}{w-u} \right)^2} \right]}{2v}. \quad (26)$$

χ is approximately 90° , so from Eqs. (20), (22), and (25) we see that q_1 corresponds to the antisymmetric stretch mode, while q_2 and q_3 correspond approximately to the symmetric stretch and bending vibration modes, respectively.

The differential equations are still coupled through the matrix S_x , part of the W_2 term. We can bring S_x into diagonal form with an equivalence transformation that takes S_x into L_x with

$$L_x = U_x S_x U_x^{-1} \quad (27)$$

(see Ref. [23]).

Finally, for the δ -order Schrödinger equation we have

$$\frac{1}{2} \left(\left[-\frac{\partial^2}{\partial q_1^2} - \frac{\partial^2}{\partial q_2^2} - \frac{\partial^2}{\partial q_3^2} + \omega_1^2 q_1^2 + \omega_2^2 q_2^2 + \omega_3^2 q_3^2 - \frac{3}{r_m^2 s_m^2} \right] I_x - \frac{L_x}{r_m^2 s_m t_m} \right) G_0^{L,\pi} = \epsilon_1 G_0^{L,\pi}, \quad (28)$$

where

$$G_0^{L,\pi}(q_1, q_2, q_3) = U_x \Phi_0^{L,\pi}(q_1, q_2, q_3), \quad (29)$$

$$\omega_2^2 = (u+w) - \sqrt{(w-u)^2 + 4v^2}, \quad (30)$$

and

$$\omega_3^2 = (u+w) + \sqrt{(w-u)^2 + 4v^2}. \quad (31)$$

Equation (28) consists of a set of uncoupled and separable simple harmonic differential equations for the $x+1$ components $[G_0^{L,\pi}(q_1, q_2, q_3)]_i$ of the vector $G_0^{L,\pi}(q_1, q_2, q_3)$. Hence the zeroth-order wave function is a product of three simple harmonic-oscillator wave functions, the frequencies of which are *independent of angular momentum*. Also, $[G_0^{L,\pi}(q_1, q_2, q_3)]_i$ is independent of i . The scaled energy \tilde{E} to first order, however, does depend on i and is given by

$$\tilde{E} = -\frac{1}{4r_m^2 s_m^2} + \delta \left[-\frac{3}{2r_m^2 s_m^2} + \omega_1 \left(n_a + \frac{1}{2} \right) + \omega_2 \left(n_s + \frac{1}{2} \right) + \omega_3 \left(n_\theta + \frac{1}{2} \right) + \omega_4 \left(n_4 + \frac{1}{2} \right) \right], \quad (32)$$

where

$$\omega_4 = -\frac{1}{r_m^2 s_m t_m}, \quad n_4 = \frac{L+1-\gamma_2-2i}{2}, \quad (33)$$

with i ranging from 1 to $x+1$. Or we can write

$$\begin{aligned} 1 \leq i \leq L+1 & \text{ for the } \pi = (-1)^L \text{ states,} \\ 1 \leq i \leq L & \text{ for the } \pi = (-1)^{L+1} \text{ states.} \end{aligned} \quad (34)$$

Also n_a , n_s , and n_θ are the number of quanta in the anti-symmetric stretch, symmetric stretch, and bending vibration modes, respectively. Finally, in order to satisfy the Pauli principle, the total spin S must satisfy

$$\begin{aligned} S=1 & \text{ when } n_a + \gamma_2 + i - 1 \text{ is odd,} \\ S=0 & \text{ when } n_a + \gamma_2 + i - 1 \text{ is even.} \end{aligned} \quad (35)$$

III. THE FULL SCHRÖDINGER EQUATION AND ITS SOLUTION

Up to this point we have found the zeroth-order wave function and the zeroth- and first-order energies. We have also defined three quantum numbers in the large- D limit, which we can choose according to which state we would like to calculate in three dimensions. For example, we would like to find the energies and wave functions for the $1s2p^1P^o$ and $1s2p^3P^o$ states. We know that these are the lowest-lying states with P^o symmetry, so we choose the smallest possible values for $\{n_a, n_s, n_\theta\}$, which would be $\{0,0,0\}$. Also we know that for P^o we have $L=1$ and $\pi=-1$; thus $\gamma_2=0$ and $x=1$. Thus the wave function $G_0^{L,\pi}$ will be a column vector with two elements so that i will take the values $i=1$ and $i=2$ [see Eq. (34)]. Finally, from Eq. (35), we have that $i=2$ for the $1s2p^3P^o$ state and $i=1$ for the $1s2p^1P^o$ state. $G_0^{L,\pi}$ then becomes a column vector with all elements equal

to zero except the i th, which becomes a product of three harmonic-oscillator functions with quantum numbers n_a , n_s , and n_θ .

After transforming the full Schrödinger equation to symmetry coordinates and then to normal coordinates and finally applying the transformation of Eqs. (27) and (29) to the entire Hamiltonian and wave function, respectively, we obtain a set of coupled differential equations that can be solved recursively at each order of $\delta^{1/2}$. The method of choice is the matrix method, developed by Dunn *et al.*, which has been discussed in detail for the one degree of freedom case [33]. Derivations for the three degree of freedom case result in very similar equations and will be discussed in a future paper. The application of the matrix method gives us the energy series and the wave function series. The next step is the summation of these series.

IV. SUMMATION OF THE ENERGY SERIES

The energy series obtained are divergent, so we cannot simply sum them in the usual way. Instead we use linear Padé approximants to sum the energy series. Padé approximants are ratios of polynomials in the expansion parameter δ . The “diagonal sequence” consists of the Padé approximants whose numerator and denominator are polynomials up to order n in δ , denoted $[n/n]$. Similarly, off-diagonal sequences are labeled $[n/n+1]$, $[n+1/n]$, etc. Due to the presence of the polynomial in the denominator the Padé approximants can model poles of the energy function. Also, by arranging poles and zeros in a particular way in the complex plane, Padé approximants can even model more complicated singularities such as square-root branch points and essential singularities [34].

We accelerate the convergence of the Padé approximants by analyzing the singularity structure of the energy series as modeled by the approximants. It was found that the Padé approximants were placing a *second-order pole* at $\delta = \frac{1}{2}$ ($D=1$). If we multiply the energy series by the factor $(\delta-1/2)^2$ and sum the resulting series at $\delta = \frac{1}{2}$ we determine that the residue of the second order pole at $\delta = \frac{1}{2}$ is equal to $-\frac{1}{2}$. Finally, we subtract from the original energy series the term $-\frac{1}{2}[1/(\delta-1/2)^2]$, essentially subtracting off the pole at $\delta = \frac{1}{2}$ ($D=1$). This new series sums much better, agreeing with other results to four decimal places (five significant figures) for both P^o states under consideration.

We improve these results by looking at the singularity

TABLE I. Energies of the $1,3P^o$ and $1,3D^o$ states calculated from the 27th-order Padé summation along with energies calculated elsewhere.

State	KT quantum numbers	Energy (au)
$1s2p\ ^3P^o$		-2.133 162 4 -2.133 164 19 ^a
$1s2p\ ^1P^o$		-2.123 843 0 -2.123 843 08 ^a
$2p3d\ ^1D^o$	${}_n(K,T)_N^A = {}_2(0,1)_3^0$	-0.563 800 39 -0.563 800 40 ^b
$2p3d\ ^3D^o$	${}_n(K,T)_N^A = {}_2(0,1)_3^0$	-0.559 328 260 -0.559 328 25 ^b

^aSee Ref. [35].

^bSee Ref. [36].

structure of the Padé approximants after having subtracted off the pole at $\delta = \frac{1}{2}$ ($D=1$). For both states the Padés place a *first-order pole* at $\delta = -\frac{1}{2}$ ($D=-3$). Previous work by Doren and Herschbach [30] has shown that we should expect a second-order pole at $D=-3$, but rather we find a first-order pole. In a similar manner we determine the residue (from the $[n+1/n]$ Padé) of this pole and subtract it. The numbers we obtain give us one additional decimal place of agreement. The results for the $1s2p\ ^{1,3}P^o$ states and their interdimensionally degenerate counterparts, the $2p3d\ ^{3,1}D^o$ states, respectively, are shown in Table I.

V. CONCLUSION

Once the formalism is developed for calculating the energies and wave functions of the $1,3P^o$ states of helium it is fairly straightforward to calculate other states. Future work will include a further analysis of the states discussed in this paper including summation of the wave-function series. We will also be able to obtain the energy and wave-function series of states with *any* value of L limited only by the amount of computer RAM. In addition, we can easily calculate series for a heliumlike atom such as Li^+ simply by changing the nuclear charge.

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