Quantum-number dimensional-scaling analysis for excited states of multielectron atoms

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A dimensional-scaling method for the calculation of excited states of multielectron atoms is introduced. By including the principle and orbital quantum numbers in the dimension parameter, we obtain an energy expression for excited states including high angular momentum states. The method is tested on He, Li, and Be. We obtain good agreement with more orthodox quantum mechanical treatments even in the zeroth order.

I. INTRODUCTION

The dimensional-scaling (D-scaling) method originally developed by Witten [1] and Herschbach [2] is now a well established technique in atomic physics [3]. Substantial progress has been made in improving the accuracy of the technique and extending it to excited states. Most notable are the approaches of Goodson and Herschbach [4–6] and the dimensional perturbation theory (DPT) developed by Carzoli, Dunn, and Watson [7,8]. In the present work, an alternative approach to generalized D scaling is developed which does not require calculations of high order $1/D$ corrections in order to obtain high-angular momentum states unlike, for example, the Padé approximate used by Goodson which required 20 orders of $1/D$. Our approach is simple and yet accurate. It predicts excited states of helium (the canonical multielectron problem) and is easily extended to N electron atoms. We demonstrate the straightforward extension by analyzing lithium and beryllium.

II. TWO APPROACHES TO D SCALING

In this section, we will review the traditional D-scaling approach for helium and introduce our alternative quantum-number dimensional formulation.

A. Traditional D scaling for helium

The Hamiltonian for helium, in atomic units, is given by

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + V(r_1, r_2, \theta), \qquad (1)$$

where

$$V(r_1, r_2, \theta) = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta}} \qquad (2)$$

is the Coulomb potential energy, θ is the angle between the electron radii vectors, and Z is the nuclear charge. The Laplacian operator, for **S** states, can be written in D dimensions as

$$\nabla_1^2 + \nabla_2^2 = K_{D-1}(r_1) + K_{D-1}(r_2) + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right) L_{D-1}^2, \qquad (3)$$

where

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$$K_{D-1}(r) = \frac{1}{r^{D-1}} \frac{\partial}{\partial r} r^{D-1} \frac{\partial}{\partial r}, \qquad (4a)$$

$$L_{D-1}^2 = \frac{1}{\sin^{D-2}\theta} \frac{\partial}{\partial\theta} \sin^{D-2}\theta \frac{\partial}{\partial\theta}. \qquad (4b)$$

The probability distribution function in D dimensions is defined to be $|\Phi_D|^2 = J_D |\Psi_D|^2$ where the D-dimensional Jacobian is given by

$$J_D = (r_1 r_2)^{D-1} \sin^{D-2}\theta \qquad (5)$$

and Ψ_D is a solution to Eq. (1) with eigenvalue E. Letting Eq. (3) act on $\Psi_D = J_D^{-1/2}\Phi_D$ and transforming parameters as

$$r_i \to \frac{(D-1)^2}{4} r_i, \qquad (6a)$$

$$E \to \frac{4}{(D-1)^2} E \qquad (6b)$$

we obtain the $D \to \infty$ limit of the energy

$$E_\infty = \frac{1}{2}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\frac{1}{\sin^2\theta} + V(r_1, r_2, \theta). \qquad (7)$$

When this energy expression is minimized with respect to the parameters (r_1, r_2, θ), an estimate of the ground state $(1s^2)$ energy of helium can be obtained which is 5% accurate. The accuracy can be improved by the $1/D$ expansion. The limitation of this approach is that expression (7) cannot produce excited **S** states nor higher-angular momentum states (states with $L > 0$) in its current form without resorting to Langmuir vibrations and high order $1/D$ corrections.

B. Present D scaling for helium

Motivated by the approach of the previous section and to avoid high order dimensional perturbation expansions, we invented a generalized Laplacian of the form

$$\nabla_1^2 + \nabla_2^2 = K_{\gamma_1}(r_1) + K_{\gamma_2}(r_2) + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right) L_\alpha^2, \qquad (8)$$

where γ_1, γ_2, and α are three different parameters which we also assume will tend toward ∞. Without loss of generality, we then factor our parameters into a finite integer part multiplied by a dimensional term given by

$$\gamma_1 = n_1(D-1), \tag{9a}$$

$$\gamma_2 = n_2(D-1), \tag{9b}$$

$$\alpha = L(D-2). \tag{9c}$$

Thus, γ_i and α will tend toward ∞ faster than D provided n_i and L are finite positive integers greater than 1. By introducing the parameters n_i and L, into the usual D-dimensional Laplacian, we will have additional degrees of freedom in the final energy expression. This parametrization can be interpreted as being the cardinality of a space larger than D dimensions which includes the energy levels of the physical system. We will refer to this space as quantum-number dimensional space. If we need to recover the usual three-dimensional Laplacian, we can add a second term to Eq. (9) given by

$$\gamma_1 = n_1(D-1) + 6(1-n_1)/D, \tag{10a}$$

$$\gamma_2 = n_2(D-1) + 6(1-n_2)/D, \tag{10b}$$

$$\alpha = L(D-2) + 3(1-L)/D. \tag{10c}$$

This parametrization allows us to recover the usual three-dimensional Schrödinger equation when $D=3$. But for large values of D, system (9) and system (10) are the same. In $\gamma - \alpha$ space, the corresponding Jacobian factor now reads

$$J_{\gamma-\alpha} = r_1^{\gamma_1} r_2^{\gamma_2} \sin^\alpha \theta \tag{11}$$

which is chosen to provide consistency with the traditional approach. If we now solve $\hat{H}\Psi_{\gamma-\alpha} = E\Psi_{\gamma-\alpha}$ with definitions (8) and (9), and the scaling transformation (6) we obtain the final energy expression in the $D \to \infty$ as

$$E = \frac{1}{2}\left(\frac{n_1^2}{r_1^2} + \frac{n_2^2}{r_2^2}\right) + \frac{L^2}{2}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\cot^2\theta + V(r_1, r_2, \theta). \tag{12}$$

The derivation of this expression is given in Appendix A. Additionally, in Appendix B we show how to correct the energy with the first $1/D$ correction. Equation (12) will allow us to obtain atomic excited states by associating n_i as the principle quantum number for electron i and L as the sum of the individual hydrogenic assignment orbital quantum numbers, i.e., $L = l_1 + l_2$. Thus, our L is the maximum in the set of possible total orbital angular momenta $\mathbf{L} \in \{|l_1 - l_2|, \ldots, |l_1 + l_2|\}$.

III. GROUND STATE AND EXCITED *S* STATES

The excited *S* states of helium can easily be found by setting $L=0$ in expression (12), we find

$$E = \frac{1}{2}\left(\frac{n_1^2}{r_1^2} + \frac{n_2^2}{r_2^2}\right) + V(r_1, r_2, \theta). \tag{13}$$

It is interesting to note that this energy expression is identical to what one would obtain for a Bohr model of helium using

TABLE I. Energy (in atomic units) of the He atom obtained using Eq. (13) for states with $L=0$. The final column is the percent error between our energy and previously published results.

$|n_1 n_2 L\rangle$	Assignment	$-E$ (present)	$-E^{a}$	Δ (%)
$|110\rangle$	$1s^2\ {}^1S$	3.0625	2.9037	5.40
$|120\rangle$	$1s2s\ {}^1S$	2.1595	2.1460	0.60
$|130\rangle$	$1s3s\ {}^1S$	2.0621	2.0613	0.03
$|140\rangle$	$1s4s\ {}^1S$	2.0333	2.0336	0.02

[a]Complex rotation technique [14].

the Bohr space quantization condition for the kinetic energy operators, i.e., $2\pi r = n\lambda$, where λ is the de Broglie wavelength $\lambda = h/p$. Bohr space quantization was also used by Greenspan [9] to obtain an energy expression for the excited states of helium but with a potential function that was parametrized. More recently, the Bohr model has been successfully applied to molecules [10–13]. Here, we take the electron-nuclear and electron-electron interaction to have their usual Coulombic form. The results for excited **S** states are presented in Table I. We see that a dominant feature is the increase in accuracy with larger quantum number n_2. This can easily be explained in terms of Bohr correspondence. Physically, as $n_2 > n_1(=1)$ the corresponding radii will be very different since $r_i \sim n_i^2$. Thus, electron two sees a screened nucleus of charge $Z=1$ and therefore it is a hydrogenic problem, which is exactly soluble in the Bohr picture.

IV. EXCITED *P* AND *D* STATES

Our goal here is to stay within the geometric configuration picture originally established by Herschbach and co-workers. Other groups have also made substantial contributions (see Ref. [3], and references therein) to use D scaling for these states. We present here a true Lewis structure picture for helium excited states thus providing an example of a classical analog for *P* states. Physically, the *P* and *D* states are just special configurations of the two electron system in hyperspherical coordinates. Table II compares the energy of the He atom for some states with $L>0$ obtained in the present analysis with the accurate values known in the literature. Table III shows the configurations of the electrons for some representative states. We have found that pure *S* states

TABLE II. Energy of thee He atom for states with $L>0$.

$|n_1 n_2 L\rangle$	Assignment	$-E$ (present)	$-E$ (Ref.)	Δ (%)
$|121\rangle$	$1s2p\ {}^1P$	2.12710	2.12380[a]	0.20
$|131\rangle$	$1s3p\ {}^1P$	2.05573	2.05514[a]	0.020
$|132\rangle$	$1s3d\ {}^1D$	2.05572	2.05562[a]	0.004
$|221\rangle$	$2s2p\ {}^1P$	0.69720	0.69310[b]	0.60
$|222\rangle$	$2p2\ {}^1D$	0.68440	0.68641[b]	0.29
$|231\rangle$	$2s3p\ {}^1P$	0.55990	0.56384[b]	0.70

[a]Reference [15].
[b]Reference [16].

TABLE III. Positions of the electrons on the hypersphere for certain representative states.

$|n_1 n_2 L\rangle$	r_1	r_2	θ
$|121\rangle$	0.5005	3.8981	90.4526°
$|132\rangle$	0.5000	8.9579	90.0221°
$|222\rangle$	2.4278	2.4278	95.3006°
$|231\rangle$	2.0249	7.9728	95.8483°

admit an angle of 180° whereas states with P character and higher-angular momenta typically lie in the range of 90° $< \theta < 180°$. We cannot, with this method, distinguish between singlet and triplet states of helium nor can we determine the correct spectroscopic assignment of **L**. We note that in general, our method finds a value somewhere near the average of the various **L** states. For example, the $2p^2 \, ^1S^e$ state energy is ≈ -0.62 a.u., whereas for the $2p^2 \, ^3P^e$ state $E \approx -0.71$ a.u. and the average of the two yields -0.67 a.u., which is much closer to our result of -0.68 a.u. However, our calculated energy is only 0.29% different from the ^1D state. This suggests that our L is indeed the sum of the individual l_i's.

Our advantage over the dimensional perturbation treatment is twofold. First, in order to calculate the excited states of helium they needed to invoke harmonic oscillator wave functions as an ansatz to the problem. The various excited modes of the normal coordinates corresponded to the hydrogenic excited states of helium. Their harmonic oscillator quantum numbers were associated with the radial and orbital nodes of the hydrogenic wave functions (see, for example, Ref. [17]). In order to calculate with this method, many orders of $1/D^n$ (in the $1/D$ expansion) were required. Furthermore, it was seen that the $1/D$ series was asymptotic and required further resummation via Padé approximates. The second drawback was the fact that it could only consider states where $l_1 = l_2$. Thus, the $1s2p$ state is not accounted for in their treatment.

The states with electron 1 in an s orbit and electron 2 in a higher-angular momentum state seem to work the best. We can correct the errors by considering small vibrations about the "frozen" configuration positions. The derivation of the first $1/D$ correction and its application are provided in Appendix B for the excited states of helium.

V. GENERALIZATION TO THE *N*-ELECTRON SYSTEM

The present approach admits a simple generalization to the N-electron atom with nuclear charge Z. We can describe the N-electron system by including all pairwise interactions. The problem will thus involve $(1/2)N(N+1)$ parameters. Let

$$K_{\gamma_i} = \frac{1}{r^{\gamma_i}} \frac{\partial}{\partial r_i} \left(r_i^{\gamma_i} \frac{\partial}{\partial r_i} \right) \quad (14)$$

as before and

TABLE IV. Results for various excited states of lithium.

$|n_1 l_1 n_2 l_2 n_3 l_3\rangle$	Assignment	$-E$ (present)	$-E$ (Ref.)	Δ (%)
$|101021\rangle$	$1s^2 2p \, ^2P$	7.6897	7.4101[a]	3.70
$|102021\rangle$	$1s2s2p \, ^4P$	5.2715	5.4375[b]	3.10
$|102121\rangle$	$1s2p^2 \, ^1D$	5.1982	5.2335[c]	0.70
$|102130\rangle$	$1s2p3s \, ^1P$	5.0744	5.0820[d]	0.15
$|102131\rangle$	$1s2p3p \, ^1P$	5.0668	5.0651[c]	0.03
$|102141\rangle$	$1s2p4p \, ^3S$	5.0395	5.0311[c]	0.16
$|202032\rangle$	$2s^2 3d \, ^3P$	1.9496	1.9690[e]	1.00
$|212132\rangle$	$2p^2 3d \, ^3P$	1.8192	1.8246[e]	0.30

[a]Reference [18].
[b]Reference[19].
[c]Reference [20].
[d]Reference [21].
[e]Reference [22].

$$L_{\alpha_{ij}}^2 = \frac{1}{\sin^{\alpha_{ij}} \theta_{ij}} \frac{\partial}{\partial \theta_{ij}} \left(\sin^{\alpha_{ij}} \theta_{ij} \frac{\partial}{\partial \theta_{ij}} \right) \quad (15)$$

then

$$\hat{H} = -\frac{1}{2} \left[\sum_{i=1}^N K_{\gamma_i} + \sum_{i<j}^N \left(\frac{1}{r_i^2} + \frac{1}{r_j^2} \right) L_{\alpha_{ij}}^2 \right]$$
$$- Z \sum_{i=1}^N \frac{1}{r_i} + \sum_{i<j}^N (r_i^2 + r_j^2 - 2 r_i r_j \cos \theta_{ij})^{-1/2}. \quad (16)$$

Here γ_i is as before and $\alpha_{ij} = L_{ij}(D-2)$ with $L_{ij} = l_i + l_j$. Next we transform the N particle wave function as

$$|\Psi\rangle = \prod_{i=1}^N r_i^{-\gamma_i/2} \prod_{i<j}^N \sin^{-\alpha_{ij}/2} \theta_{ij} |\Phi\rangle. \quad (17)$$

Transforming $|\Psi\rangle$ in this way makes the analysis a natural continuation of the helium problem with the exception that the angular momentum are multiply counted. Then in the large-D limit the energy function to be minimized is

$$E(n_1 l_1 n_2 l_2 \cdots n_N l_N)$$
$$= \frac{1}{2} \sum_{i=1}^N \frac{n_i^2}{r_i^2} + \frac{1}{2} \left(\frac{1}{N-1} \right) \sum_{i<j} L_{ij}^2 \left(\frac{1}{r_i^2} + \frac{1}{r_j^2} \right) \cot^2 \theta_{ij} + V(\vec{r}, \vec{\theta}),$$
$$(18)$$

where

$$V(\vec{r}, \vec{\theta}) = - Z \sum \frac{1}{r_i} + \sum_{i<j} (r_i^2 + r_j^2 - 2 r_i r_j \cos \theta_{ij})^{-1/2}. \quad (19)$$

The factor of $1/(N-1)$ accounts for the multiple counting of each l_i. For the case of the ground state of lithium ($Z=3$, $N=3$) in the state $1s^2 2s$ we obtain $E = -7.7468$ which is 3.5% different from the true ground state of -7.4780. However, the accuracy of higher states (including $l_i > 0$) is typically much better (see Table IV). Additionally, we tested the method on beryllium and had some success. In this study, we considered states with the core electrons fixed in the $1s^2$ orbits. We

TABLE V. Ground state and various excited states of beryllium. Core electrons $1s^2$ are implicit in the notation. The percent error is with respect to the corrected value column.

$|n_3 l_3 n_4 l_4\rangle$	Assignment	$-E$ (present)	Corrected	$-E^{\mathrm{a}}$	Δ (%)
$|2020\rangle$	$2s^2\,^1S$	15.0603	14.6673	14.6673	0.00
$|2021\rangle$	$2s2p\,^1P$	14.8939	14.5009	14.4734	0.20
$|2030\rangle$	$2s3s\,^1S$	14.8014	14.4084	14.4182	0.07
$|2121\rangle$	$2p^2\,^1D$	14.7674	14.3744	14.4079	0.23
$|2031\rangle$	$2s3p\,^1P$	14.7693	14.3763	14.3931	0.11
$|2032\rangle$	$2s3d\,^1D$	14.7682	14.3752	14.3737	0.01

$^{\mathrm{a}}$References [23], [24], and [25].

found an error with respect to published values of 2.6%. To eliminate this systematic error, we subtracted off the ground state error from each of the excited states and found very good agreement with published results. Shown in Table V are some calculated excited states of beryllium which are compared to other published results.

VI. CONCLUSION

We have introduced an alternative form of dimensional scaling for the excited states of atoms. By treating the principle and orbital quantum numbers to be innately coupled to the dimension D, we developed an algebraic equation for multiple excited states of multielectron atoms including states of high orbital momentum. This method can be extended to include relativistic effects for nuclei with high Z numbers by including the kinetic-energy mass correction term of the Breit-Pauli Hamiltonian.

ACKNOWLEDGMENTS

APPENDIX A: SCHRÖDINGER EQUATION IN D DIMENSIONS

Here we demonstrate the idea of our D-scaling transformation by applying it to the He atom. The Hamiltonian of He in three dimensions is given by Eq. (1). First we perform a continuous transformation of the Laplacian as follows:

$$\nabla_1^2 + \nabla_2^2 = \frac{1}{r_1^{\gamma_1}}\frac{\partial}{\partial r_1}r_1^{\gamma_1}\frac{\partial}{\partial r_1} + \frac{1}{r_2^{\gamma_2}}\frac{\partial}{\partial r_2}r_2^{\gamma_2}\frac{\partial}{\partial r_2}$$
$$+ \left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\frac{1}{\sin^\alpha\theta}\frac{\partial}{\partial\theta}\sin^\alpha\theta\frac{\partial}{\partial\theta}, \quad \text{(A1)}$$

where γ_1, γ_2, and α are given by Eqs. (9). The wave function, coordinates, and the energy transform according to

$$\Psi = [r_1^{\gamma_1} r_2^{\gamma_2} \sin^\alpha\theta]^{-1/2}\Phi, \quad r_i \to \frac{(D-1)^2}{4}r_i,$$

$$E \to \frac{4}{(D-1)^2}E. \quad \text{(A2)}$$

The radial part of the Laplacian acting on Ψ yields

$$\frac{1}{r^\gamma}\frac{\partial}{\partial r}\left(r^\gamma\frac{\partial\Psi}{\partial r}\right) = r^{-\gamma/2}\sin^{-\alpha/2}\theta\left[\frac{\partial^2}{\partial r^2} - \left(\frac{\gamma}{2}\right)\left(\frac{\gamma-2}{2}\right)\frac{1}{r^2}\right]\Phi, \quad \text{(A3)}$$

while the angular part leads to

$$\frac{1}{\sin^\alpha\theta}\frac{\partial}{\partial\theta}\left(\sin^\alpha\theta\frac{\partial\Psi}{\partial\theta}\right)$$
$$= r^{-\gamma/2}\sin^{-\alpha/2}\theta\left[\frac{\partial^2}{\partial\theta^2} + \frac{\alpha}{2} - \left(\frac{\alpha}{2}\right)\left(\frac{\alpha-2}{2}\right)\cot^2\theta\right]\Phi. \quad \text{(A4)}$$

After the transformation the Schrödinger equation reduces to

$$(T + U + V)\Phi = E\Phi, \quad \text{(A5)}$$

where

$$T = -\frac{2}{(D-1)^2}\left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\frac{\partial^2}{\partial\theta^2}\right] \quad \text{(A6)}$$

is the kinetic energy term and

$$U = \frac{\gamma_1(\gamma_1-2)}{2(D-1)^2}\frac{1}{r_1^2} + \frac{\gamma_2(\gamma_2-2)}{2(D-1)^2}\frac{1}{r_2^2} + \left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)$$
$$\times\left[\frac{\alpha(\alpha-2)}{2(D-1)^2}\cot^2\theta - \frac{\alpha}{(D-1)^2}\right] \quad \text{(A7)}$$

is the centrifugal potential. In the large-D limit the kinetic energy term vanishes and Eq. (A5) reduces to finding the minimum of the algebraic energy function (12).

APPENDIX B: CALCULATION OF $1/D$ CORRECTION

Let us take into account terms of the order of $1/D$ in Eq. (A5), then it reduces to

$$\left\{-\frac{2}{D^2}\left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\frac{\partial^2}{\partial\theta^2}\right]\right.$$
$$+ \frac{1}{2}\left(\frac{n_1^2}{r_1^2}+\frac{n_2^2}{r_2^2}\right) + \frac{L^2}{2}\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\cot^2\theta + V$$
$$\left. - \frac{1}{D}\left[\frac{n_1}{r_1^2}+\frac{n_2}{r_2^2} + \left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)[L(L+1)\cot^2\theta + L]\right]\right\}\Phi$$
$$= E\Phi. \quad \text{(B1)}$$

We decompose the effective potential $U+V$ in Eq. (B1) near the minimum $(r_{10}, r_{20}, \theta_0)$ and leave only terms quadratic in displacement from this point. As a result, we obtain

$$\left\{ E_\infty - \frac{1}{D}\left[\frac{n_1}{r_{10}^2} + \frac{n_2}{r_{20}^2} + \left(\frac{1}{r_{10}^2} + \frac{1}{r_{20}^2} \right)[L(L+1)\cot^2\theta_0 + L] \right] \right\}\Phi$$

$$- \frac{2}{D^2}\left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \left(\frac{1}{r_{10}^2} + \frac{1}{r_{20}^2} \right)\frac{\partial^2}{\partial\theta^2} \right]\Phi$$

$$+ [\beta_{11}\Delta r_1^2 + \beta_{22}\Delta r_2^2 + \beta_{33}\Delta\theta^2 + 2\beta_{12}\Delta r_1\Delta r_2$$

$$+ 2\beta_{13}\Delta r_1\Delta\theta + 2\beta_{23}\Delta r_2\Delta\theta]\Phi = E\Phi, \tag{B2}$$

where β_{ij} are coefficients of the Taylor expansion of the function $U+V$ at the minimum. Equation (B2) describes three coupled one dimension harmonic oscillators. To make the oscillator masses equal we rescale $\Delta\theta$ as $\Delta\theta = \Delta\tilde{\theta}/r_0$, where $1/r_0 = \sqrt{1/r_{10}^2 + 1/r_{20}^2}$. Then Eq. (B2) yields

$$\left\{ E_\infty - \frac{1}{D}\left[\frac{n_1}{r_{10}^2} + \frac{n_2}{r_{20}^2} + \left(\frac{1}{r_{10}^2} + \frac{1}{r_{20}^2} \right)[L(L+1)\cot^2\theta_0 + L] \right] \right\}\Phi$$

$$- \frac{2}{D^2}\left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \frac{\partial^2}{\partial\tilde{\theta}^2} \right]\Phi + [\beta_{11}\Delta r_1^2 + \beta_{22}\Delta r_2^2$$

$$+ \beta_{33}\Delta\tilde{\theta}^2/r_0^2 + 2\beta_{12}\Delta r_1\Delta r_2 + 2\beta_{13}\Delta r_1\Delta\tilde{\theta}/r_0$$

$$+ 2\beta_{23}\Delta r_2\Delta\tilde{\theta}/r_0]\Phi = E\Phi. \tag{B3}$$

The problem is reduced to determining eigenvalues Λ_1, Λ_2, Λ_3 of the symmetric matrix

$$\begin{pmatrix} \beta_{11} & \beta_{12} & \beta_{13}/r_0 \\ \beta_{12} & \beta_{22} & \beta_{23}/r_0 \\ \beta_{13}/r_0 & \beta_{23}/r_0 & \beta_{33}/r_0^2 \end{pmatrix}.$$

The energy including the $1/D$ correction is then given by

TABLE VI. Improvement after the first $1/D$ correction.

State	Zeroth order	First order
$1s^2\,{}^1S$	5.40%	1.67%
$2s3p\,{}^1P$	0.70%	0.54%

$$E = \frac{4}{(D-1)^2}\left\{ E_\infty - \frac{1}{D}\left[\frac{n_1}{r_{10}^2} + \frac{n_2}{r_{20}^2} + \left(\frac{1}{r_{10}^2} + \frac{1}{r_{20}^2} \right) \right.\right.$$

$$\times (L(L+1)\cot^2\theta_0 + L)\Big]$$

$$\left. + \frac{\sqrt{2}}{D}[\sqrt{\Lambda_1} + \sqrt{\Lambda_2} + \sqrt{\Lambda_3}] \right\}. \tag{B4}$$

We have applied Eq. (B4) to correct the energy we found for the $1s^2$ state from Table I and the $2s3p$ state from Table II. Shown in Table VI is a comparison between the zeroth order and first $1/D$ correction for these states with respect to the more exact values. We have noticed that it is possible to correct the energy with the $1/D$ expansion to first order but only if the zeroth order error is significant. For states where the zeroth order gave very good accuracy (i.e., 1%) we do not expect much improvement from the first $1/D$ correction. It was noted in Ref. [3] that 30 terms of the $1/D$ expansion leads to a nine decimal place accuracy for the ground state energy of helium. Thus, the first order term should only correct the most significant figure.

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