PHYSICAL REVIEW E VOLUME 62, NUMBER 3 SEPTEMBER 2000

Calculation of the first excited ${}^1S^e$ state of the He atom using supersymmetric quantum mechanics and extension to the nth excitation

Tapan Kumar Das,* and Barnali Chakrabarti†
Department of Physics, University of Calcutta, 92 Acharya Prafulla Chandra Road, Calcutta 700009, India

(Received 3 January 2000; revised manuscript received 1 June 2000)

Usually the renormalized Numerov (RN) algorithm is used to solve the set of coupled differential equations of the few-body system, mainly for the ground state. The straightforward approach of this algorithm faces some serious problems of convergence to calculate the excited states. Here we present an alternative method using the supersymmetric quantum mechanics formalism to a multidimensional bound-state problem. The problem of convergence is avoided in this approach by searching for the ground state of the partner potential. Application of this formalism to the first excited ${}^1S^e$ state of the He atom gives excellent results; it is much better than the conventional RN algorithm and the hyperspherical adiabatic approximation. We also indicate how the method can be generalized to the nth excited state.

PACS number(s): 02.60.−x, 31.15.Ar, 31.25.−v, 03.65.−w

I. INTRODUCTION

The hyperspherical harmonics expansion (HHE) method has been successfully used to obtain the ground states of two electron atoms and ions [1–8]. This method results in a set of coupled differential equations (CDE). The numbers (N) of the set of CDE depends on the extent of truncation of the hyperspherical expansion basis. Since the Coulomb force is a long-ranged one, the convergence of the hyperspherical expansion is slow and N is usually fairly large ($\sim$100) for a reasonable precision. The set of CDE has to be solved numerically, subject to appropriate boundary condition. Usually the renormalized Numerov (RN) algorithm [9] is used to solve the set of CDE for the ground state. A straightforward adoption of this algorithm for the excited states is faced with some serious problems in the convergence of the iterative RN procedure. In this paper, we present an alternative method using supersymmetric quantum mechanics (SSQM) for the excited states. For a one-dimensional Schrödinger equation with a potential V_1, in which the energy scale is shifted in such a way that the ground state is at zero energy, one can define a superpotential W. This W is proportional to ψ_0'/ψ_0, where ψ_0 is the ground-state wave function. Using this superpotential, one can define a partner potential V_2. It can be shown that both V_1 and V_2 have identical energy spectra, except that the ground state of V_1 is missing in the spectrum of V_2 [10]. Corresponding eigenfunctions are also related through the operator $A^\dagger$ (A), which creates (destroys) a node of the wave function. Thus the first excited state of V_1 can be computed by first calculating V_2 and then looking for its ground state. Although the procedure is straightforward and the formalism is known for a couple of decades for a one-dimensional problem, a generalization to a multidimensional bound-state problem or equivalently to a system of N coupled differential equations in one variable has only been proposed recently by us [11], using a matrix superpotential. We apply this formalism to the first excited ${}^1S^e$ state of the helium atom and obtain numerical results. Furthermore, we discuss how the method can be generalized to the nth excited state.

This paper is organized as follows. In Sec. II, we briefly describe the hyperspherical harmonics expansion method. The SSQM formalism for a set of CDE is briefly reviewed in Sec. III. In Sec. IV, we apply this formalism to the first excited state of the helium atom. In Sec. V, we indicate how the method can be generalized to higher excited states with the same symmetry. Finally, we draw our conclusions in Sec. VI.

II. HYPERSPHERICAL HARMONICS EXPANSION METHOD FOR A THREE-BODY SYSTEM

We label the two electrons (mass m, charge $-e$) as particles 1 and 2, and the nucleus (mass M, charge $+Ze$) as particle 3. Then the Schrödinger equation has the form [8]

$$\left[-\frac{\hbar^2}{2m}(\nabla^2_{r_1}+\nabla^2_{r_2})-\frac{\hbar^2}{2M}\nabla^2_{r_3}-Ze^2\left(\frac{1}{|\vec{r}_1-\vec{r}_3|}+\frac{1}{|\vec{r}_2-\vec{r}_3|}\right)+\frac{e^2}{|\vec{r}_1-\vec{r}_2|}-E_{\rm tot}\right]\psi(\vec{r}_1,\vec{r}_2,\vec{r}_3)=0. \tag{1}$$

We introduce the Jacobi coordinates

$$\vec{\xi}_1=a_1(\vec{r}_2-\vec{r}_1),$$
$$\vec{\xi}_2=a_2\left[\vec{r}_3-\frac{\vec{r}_1+\vec{r}_2}{2}\right], \tag{2}$$
$$\vec{R}=[m(\vec{r}_1+\vec{r}_2)+M\vec{r}_3]/(M+2m),$$

where $a_1=[(M+2m)/2M]^{1/2}$, $a_2=1/a_1$, and $\vec{R}$ is the center-of-mass coordinate. With the transformation (2), the center-of-mass motion is eliminated and the relative motion is described by

$$\left[-\frac{\hbar^2}{2\mu}(\nabla^2_{\xi_1}+\nabla^2_{\xi_2})+V-\mathcal{E}\right]\psi(\vec{\xi}_1,\vec{\xi}_2)=0, \tag{3}$$

---

*Email address: tkdas@cucc.ernet.in
†Email address: barnali@cucc.ernet.in

1063-651X/2000/62(3)/4347(4)/$15.00

where V is the sum of the three pairwise Coulomb interactions, μ is an effective mass [8] given by $\mu=[m^2M/(M+2m)]^{1/2}$, and $\mathcal{E}$ is the relative energy. Introducing hyperspherical variables

$$r=(\xi_1^2+\xi_2^2)^{1/2}, \quad \phi=\tan^{-1}\left(\frac{\xi_1}{\xi_2}\right), \tag{4}$$

and four other angles $(\vartheta_{\xi_1},\varphi_{\xi_1})$ and $(\vartheta_{\xi_2},\varphi_{\xi_2})$ which are, respectively, the spherical polar angles of $\vec{\xi}_1$ and $\vec{\xi}_2$, Eq. (3) can be written as

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r^5}\frac{\partial}{\partial r}\left(r^5\frac{\partial}{\partial r}\right)-\frac{\hat{\mathcal{K}}^2(\Omega)}{r^2}+V(r,\Omega)-\mathcal{E}\right]\psi(r,\Omega)=0, \tag{5}$$

where r is the hyperradius and the set of five angles $\{\phi,\vartheta_{\xi_1},\varphi_{\xi_1},\vartheta_{\xi_2},\varphi_{\xi_2}\}$ are collectively called hyperangles and are represented by the symbol Ω. The operator $\hat{\mathcal{K}}^2(\Omega)$ is the square of the hyperangular momentum (which is the six-dimensional analog of the ordinary three-dimensional $\hat{L}^2$ operator) satisfying an eigenvalue equation

$$\hat{\mathcal{K}}^2(\Omega)\mathcal{Y}_{K\alpha}(\Omega)=\hbar^2K(K+4)\mathcal{Y}_{K\alpha}(\Omega), \tag{6}$$

where $\alpha=(l_{\xi_1},l_{\xi_2},L,M)$ is a short-hand notation $(\vec{L}=\vec{l}_{\xi_1}+\vec{l}_{\xi_2})$. The eigenfunction $\mathcal{Y}_{K\alpha}(\Omega)$ is known as hyperspherical harmonics (HH). Closed analytic expressions for $\mathcal{Y}_{K\alpha}(\Omega)$ are known [12]. The wave function $\psi(r,\Omega)$ is expanded in the complete orthonormal basis of $\{\mathcal{Y}_{K\alpha}(\Omega)\}$:

$$\psi(r,\Omega)=\sum_{K\alpha}\frac{u_{K\alpha}(r)}{r^{5/2}}\mathcal{Y}_{K\alpha}(\Omega). \tag{7}$$

The factor $r^{-5/2}$ is introduced to remove the first derivative in Eq. (5). Note that r is invariant under ordinary three-dimensional rotations as also under permutations of the particle indices. Hence required symmetry of the wave function can be imposed by choosing for the expansion [Eq. (7)] a suitable subset (or linear combinations) of $\{\mathcal{Y}_{K\alpha}(\Omega)\}$ satisfying the symmetry. In our case, for the singlet states $(S_{12}=0)$, the space wave function must be symmetric under P_{12}, which requires l_{ξ_1} to be an even integer. Furthermore, if only $L=0$ states are considered, $l_{\xi_2}=l_{\xi_1}=$even integer. Substitution of Eqs. (6) and (7) in Eq. (5) and use of orthonormality of the HH's give a set of coupled differential equations:

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}+\frac{\hbar^2}{2\mu}\frac{\mathcal{L}_K(\mathcal{L}_K+1)}{r^2}-\mathcal{E}\right]u_{K\alpha}(r)+\sum_{K'\alpha'}\langle K\alpha|V(r,\Omega)|K'\alpha'\rangle u_{K'\alpha'}(r)=0, \tag{8}$$

where $\mathcal{L}_K=K+\frac{3}{2}$. This is in principle an infinite set of CDE. If the expansion [Eq. (7)] is truncated to N terms, Eq. (8) is a set of N CDE. Equation (8) can be written in a matrix form as

$$\left(-\frac{d^2}{dr^2}[I]+[V_1]-E\right)|u(r)\rangle_1=0, \tag{9}$$

where

$$(V_1)_{K\alpha,K'\alpha'}=\frac{\mathcal{L}_K(\mathcal{L}_K+1)}{r^2}\delta_{K\alpha,K'\alpha'}+\frac{2\mu}{\hbar^2}\langle K\alpha|V(r,\Omega)|K'\alpha'\rangle \tag{10}$$

and E is the energy in units of $\hbar^2/2\mu$; we express both $[V_1]$ and E in a shifted energy scale, such that the ground-state energy is zero. The energy eigenket is relabeled as $|u(r)\rangle_1$, whose components are $u_{K\alpha}(r)$. Here we adopt the notation that a symbol enclosed between square brackets represents an $N\times N$ matrix and a ket vector represents an N-component column vector. In the next section we discuss how the SSQM formalism can be adopted for the set of CDE, Eq. (9).

III. SSQM FORMULATION FOR A SET OF CDE

The ground state $|u^{(0)}\rangle_1$ of Eq. (9) (for which $E=0$ in the shifted energy scale) satisfies

$$\left(-\frac{d^2}{dr^2}[I]+[V_1]\right)|u^{(0)}\rangle_1=0. \tag{11}$$

We define a matrix superpotential $[W]$ through

$$[W]|u^{(0)}\rangle_1=-|u^{(0)\prime}\rangle_1, \tag{12}$$

where the prime indicates differentiation once with respect to the argument. Substitution of Eq. (12) and its derivative into Eq. (11) suggests the relation [11]

$$[V_1]=[W^2]-[W']. \tag{13}$$

We also define two matrix operators

$$[A]=\frac{d}{dr}[I]+[W], \qquad [A^\dagger]=-\frac{d}{dr}[I]+[W]. \tag{14}$$

Then it is easily seen that

$$[H_1]=-\frac{d^2}{dr^2}[I]+[V_1]=[A^\dagger][A] \tag{15}$$

and

$$[A]|u^{(0)}\rangle_1=0. \tag{16}$$

We can now define a partner Hamiltonian

$$[H_2]=[A][A^\dagger]=-\frac{d^2}{dr^2}[I]+[V_2] \tag{17}$$

with

$$[V_2]=[W^2]+[W']. \tag{18}$$

TABLE I. Energy of the first excited state of the helium atom calculated by SSQM and comparison with HAA and HHE results are presented. Ground-state energy calculated by HHE is also included (all energies are in atomic units).

	Ground-state energy		First excited state			
$K_{\max}$	HHE	Experiment	SSQM	HAA	HHE	Experiment
4	−2.784 371		−2.009 39	−1.592 17	−1.599 27	
8	−2.855 022	−2.903 72	−2.071 95	−1.759 05	−1.771 54	−2.138 95
12	−2.876 008		−2.079 26	−1.864 53	−1.878 54	
16	−2.887 544		−2.090 72	−1.933 78	−1.947 69	

Applying $[H_2]$ on $[A]|u^{(n)}\rangle_1$ (where $|u^{(n)}\rangle_i$ is the nth excited state of $[H_i]$, corresponding to energy $E_n^{(i)}$, $i=1,2$), one can see that $[A]|u^{(n)}\rangle_1$ is an eigenket of $[H_2]$ corresponding to energy $E_n^{(1)}$. Since Eq. (16) shows that $|u^{(0)}\rangle_1$ is annihilated by $[A]$ and $E_n^{(i)}$ increases as n increases, we have [11]

$$[A]|u^{(n+1)}\rangle_1 \propto |u^{(n)}\rangle_2 \tag{19}$$

and

$$E_{n+1}^{(1)}=E_n^{(2)} \quad (n=0,1,2,\ldots). \tag{20}$$

In a similar manner, we can see

$$[A^\dagger]|u^{(n)}\rangle_2 \propto |u^{(n+1)}\rangle_1 . \tag{21}$$

Thus we see that the energy spectrum for $[H_2]$ is identical to that of $[H_1]$, except the absence of the ground state of $[H_1]$ in the spectrum of $[H_2]$. Thus to obtain the first excited state of $[H_1]$, one can construct the superpotential matrix $[W]$, with which one can construct the partner Hamiltonian $[H_2]$ and finally look for the ground state of $[H_2]$. In the following section, we demonstrate this procedure for the first excited ${}^1S^e$ state of the helium atom.

IV. APPLICATION TO THE FIRST EXCITED ${}^1S^e$ STATE OF THE HELIUM ATOM

Using the RN algorithm [9], we solve Eq. (11) for the ground state of the helium atom as in Ref. [8]. This gives the ground state $|u^{(0)}\rangle_1$ as an N-component column vector, which is normalized to unity. Then one can verify that the following choice of a symmetrized expression for the superpotential

$$[W]=-|u^{(0)\prime}\rangle_{1\,1}\langle u^{(0)}|-|u^{(0)}\rangle_{1\,1}\langle u^{(0)\prime}| \tag{22}$$

satisfies Eq. (12). Although the form [Eq. (22)] is not unique, it is acceptable as a simple approach. In terms of this $[W]$, we can calculate the partner potential matrix $[V_2]$ using Eq. (18), given by

$$\begin{aligned}[V_2(r)]=-[B(r)]+\phi(r)[A(r)]-[V_1(r)][A(r)]\\ -[A(r)][V_1(r)],\end{aligned} \tag{23}$$

where

$$\phi(r)=-{}_1\langle u^{(0)}|[V_1(r)]|u^{(0)\prime}\rangle_1 , \tag{24}$$

$$[A(r)]=|u^{(0)}\rangle_{1\,1}\langle u^{(0)}|, \tag{25}$$

and

$$[B(r)]=|u^{(0)\prime}\rangle_{1\,1}\langle u^{(0)\prime}|. \tag{26}$$

We construct the potential matrix $[V_2]$ using Eqs. (23)–(26) and then solve the corresponding CDE,

$$\left(-\frac{d^2}{dr^2}[I]+[V_2]-E_0^{(2)}\right)|u^{(0)}\rangle_2=0, \tag{27}$$

by the same RN algorithm to obtain the ground-state energy $E_0^{(2)}$ and its eigenket $|u^{(0)}\rangle_2$. By Eq. (20), the energy of the first excited ${}^1S^e$ state of the helium atom is given by $E_0^{(2)}$, followed by a reshifting of energy to the original energy scale. In Table I, we present calculated energy of the first excited (${}^1S^e$) state of the helium atom for various $K_{\max}$ values [$K_{\max}$ is the maximum K value retained in the truncated expansion, Eq. (7)]. For each $K \leqslant K_{\max}$, all allowed values of α, consistent with the required symmetry, have been retained. In the same table, we also present the excited-state calculation by the hyperspherical adiabatic approximation (HAA) (in column 5) [8] and by the HHE method using the RN algorithm directly to $[V_1]$ [8] (in column 6). From Table I, it is seen that the convergence trend for the energy is clearly discernible and the calculated value by SSQM agrees fairly well with the experimental value and is much better than either the HAA or the HHE value for each $K_{\max}$.

V. EXTENSION TO HIGHER EXCITED STATES

Our method can easily be generalized to higher excited states. For this we start with the partner potential $[V_2]$ as our starting potential and repeat the procedure adopted for $[V_1]$, i.e., we shift the energy scale again so that the ground state of $[V_2]$ is at zero energy. Since we already know the ground-state wave function $|u^{(0)}\rangle_2$ by solving Eq. (27) numerically (the wave function remains unchanged for a constant shift in energy), we can now construct the symmetrized superpotential $[W_2]$ corresponding to the potential matrix $[V_2]$ as [in analogy with Eq. (22)]

$$[W_2]=-|u^{(0)\prime}\rangle_{2\,2}\langle u^{(0)}|-|u^{(0)}\rangle_{2\,2}\langle u^{(0)\prime}|. \tag{28}$$

We can then calculate the partner potential of $[V_2]$, viz., $[V_3]=[W_2^2]+[W_2']$. Replacing $[V_2]$ by $[V_3]$ in Eq. (27), we get the ground state ($E_0^{(3)}$) and wave function ($|u^{(0)}\rangle_3$) for the potential $[V_3]$. By an extension of the argument leading

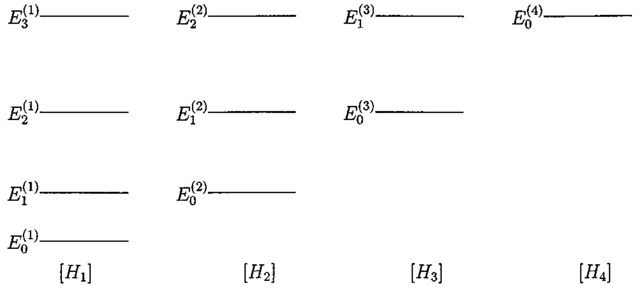

FIG. 1. Energy-level diagram of the hierarchy of Hamiltonians and their energy spectra.

to Eq. (20), we have $E_n^{(3)}=E_{n+1}^{(2)}=E_{n+2}^{(1)}$. Thus the energy of the second excited state of the original potential $[V_1]$ is obtained, by reshifting back to the original energy scale. This process can be repeated for any excited state. In this way we are constructing a hierarchy of Hamiltonians $[H_1],[H_2],[H_3],\ldots$ corresponding to potentials $[V_1],[V_2],[V_3],\ldots$ such that each successive member has the same energy spectrum as the previous member, except that the ground state of the previous member is missing in the next member of the hierarchy (Fig. 1). Thus the SSQM method can be applied recursively to any excited state.

VI. CONCLUSIONS

We have demonstrated that the formalism of SSQM for a set of coupled differential equations can be utilized profitably for the calculation of excited states of such systems. A straightforward numerical solution of the HHE equation for the excited states faces difficulties in the convergence of the numerical algorithm. This is because the excited states become gradually more spread out in the global length (r) as the excitation increases. This means that the dominant partial wave $[u_{K\alpha}(r)]$ corresponds to a larger K value as the excitation increases. The ground state has the largest contribution from the $K=0$ partial wave. Thus the rate of convergence with respect to $K_{\max}$ decreases rapidly with the excitation. This difficulty is avoided in the SSQM procedure, by always searching for the ground states of partner potentials, constructed from the ground-state solution of the preceeding Hamiltonian in the hierarchy of partner Hamiltonians. Thus in the SSQM procedure, the rate of convergence is *not* significantly slowed down, even for the excited states. This is in sharp contrast with the straightforward HHE procedure. This is clearly seen from Table I. The SSQM result even for $K_{\max}=4$ is only 6% below the experimental binding energy, while the straightforward HHE result for the same $K_{\max}$ value is 25% below the experimental value. Remembering that N (and therefore the numerical effort) increases rapidly with $K_{\max}$ [8], the improved convergence is particularly useful for the long-range Coulomb potential, for which the HHE method is known to be slowly converging. Thus the SSQM procedure outlined here is a convenient practical method for atomic problems.

ACKNOWLEDGMENT

One of us (B.C.) acknowledges support from the University Grants Commission (UGC), India.

---

[1] U. Fano, Rep. Prog. Phys. **46**, 97 (1983).
[2] U. Fano and A. R. P. Rau, *Atomic Collisions and Spectra* (Academic, New York, 1986).
[3] C. D. Lin, Adv. At. Mol. Phys. **22**, 77 (1986).
[4] C. D. Lin, Phys. Rep. **257**, 1 (1995).
[5] L. M. Delves, Nucl. Phys. **9**, 391 (1959); **20**, 268 (1962).
[6] *Few Body Methods: Principles and Applications*, edited by T. K. Lim, C. G. Bao, D. P. Hou, and S. Huber (World Scientific, Singapore, 1986), and references therein.
[7] C. D. Lin, Phys. Rev. A **29**, 1019 (1984); Phys. Rev. Lett. **51**, 1348 (1983).
[8] T. K. Das, R. Chottopadhyay, and P. K. Mukherjee, Phys. Rev. A **50**, 3521 (1994); Phys. Scr. **54**, 601 (1996).
[9] B. R. Johnson, J. Chem. Phys. **69**, 4678 (1978).
[10] L. Gendenshtein, Pis'ma Zh. Eksp. Teor. Fiz. **38**, 299 (1983) [JETP Lett. **38**, 356 (1983)]; F. Cooper, A. Khare, and U. Sukhatme, Phys. Rep. **251**, 267 (1995).
[11] T. K. Das and B. Chakrabarti, J. Phys. A **32**, 2387 (1999).
[12] J. L. Ballot and M. Fabre de la Ripelle, Ann. Phys. (N.Y.) **127**, 62 (1980).