PHYSICAL REVIEW A VOLUME 45, NUMBER 5 1 MARCH 1992

Schrödinger equation for two-electron atoms expressed in terms of symmetric sparse matrices involving only O(4,2) representations

E. de Prunelé

Service des Photons, Atomes et Molecules, Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette CEDEX, France

(Received 3 April 1991; revised manuscript received 7 October 1991)

The Schrödinger equation for two-electron atoms is replaced by another equation depending on a free dimensionless parameter β. Solution of the latter equation amounts to the diagonalization of a (β-dependent) infinite symmetric sparse matrix. The nonzero elements of this matrix are very simple and directly related to a representation of the o(4,2) algebra. Numerical results are in agreement with energy levels of the helium atom when β goes to infinity.

PACS number(s): 31.20.Tz, 31.50.+w, 34.80.−i, 03.65.Fd

I. INTRODUCTION

The use of the O(4,2) group or of one of its noncompact subgroups has proved recently to be very successful for a quantum-mechanical study of the hydrogenic diamagnetic problem (see, e.g., Refs. [1–4]). For a general and detailed review paper on the representation theory of the o(4,2) algebra and it use in physics, see, e.g., Ref. [5]. This subject is also introduced in the monograph by Condon and Odabasi [6]. This method cannot be used directly for the two-electron atomic problem. The basic reason is not the greater number of degrees of freedom that are involved in the dynamics of this latter problem. The basic reason originates from the repulsive interelectronic term $1/|\mathbf{r}-\mathbf{r}'|$. This operator or its inverse cannot indeed be expressed as a finite polynomial function of the o(4,2) generators associated (see below) with each electron.

This paper presents a way to bypass this basic difficulty. It is based on o(4,2) operator replacements [7,8]. As a result, the three-body Coulomb problem is essentially formulated in terms of diagonalization of infinite sparse symmetric matrices. The nonzero matrix elements are extremely simple and their calculation immediate. Numerical applications are carried out for some energy levels of the helium atom and illustrate the convergence of the method. The present method of o(4,2) operator replacements is quite general and can be implemented in other problems of quantum mechanics.

II. NOTATIONS AND DEFINITIONS

The Schrödinger equation for two-electron atoms in the limit of infinite nucleus mass and for nuclear Z is

$$[\tfrac{1}{2}p^2-Z/r+\tfrac{1}{2}p'^2-Z/r'+1/|\mathbf{r}-\mathbf{r}'|-E]|\Psi\rangle=0 \ . \tag{1}$$

Atomic units are used. The symbols $\mathbf{r},\mathbf{p}$ denote the position and momentum operators associated with an electron. The superscript prime refers to the other electron. The above equation can be considered within the o(4,2) algebra framework because a realization of this algebra in terms of position and momentum operators has been obtained [9]:

$$\mathbf{a}(\beta)\equiv \exp(-\beta)[\tfrac{1}{2}\mathbf{r}p^2-\mathbf{p}(\mathbf{r}\cdot\mathbf{p})]-\tfrac{1}{2}\exp(\beta)\mathbf{r} \ ,$$

$$\mathbf{l}\equiv\mathbf{r}\times\mathbf{p} \ , \quad \mathbf{g}\equiv r\mathbf{p} \ , \quad t_2\equiv rp_r, \quad \mathbf{b}(\beta)\equiv\mathbf{a}(\beta)+\exp(\beta)\mathbf{r} \ ,$$

$$t_1(\beta)\equiv\tfrac{1}{2}[\exp(-\beta)rp^2-\exp(\beta)r] \ ,$$

$$t_3(\beta)\equiv\tfrac{1}{2}[\exp(-\beta)rp^2+\exp(\beta)r] \ .$$

The above operators indeed satisfy the commutation relations characterizing an o(4,2) algebra. The usual realization of the o(4,2) algebra [9,5,6] corresponds to the above equations with $\beta=0$. The present dependence of the generators on the real dimensionless parameter β corresponds to a similarity transformation generated by t_2, for example,

$$\mathbf{a}(\beta)\equiv \exp(i\beta t_2)\mathbf{a}(0)\exp(-i\beta t_2) \ .$$

This transformation corresponds to a change of length scale by a factor $\exp(\beta)$. Clearly, this similarity transformation applied to all generators does not change the commutation relations. The o(4,2) generators are Hermitian. It is emphasized that the words Hermitian, unitary, and normalized are used throughout the present paper with respect to the $1/r$ scalar product [5] (or $1/rr'$ scalar product when both electrons are considered). The direct reformulation of the Schrödinger equation for two-electron atoms, Eq. (1), in terms of the o(4,2) generators has been up to now of little practical use, because, as indicated in Sec. I, the repulsive interelectronic term $1/|\mathbf{r}-\mathbf{r}'|$ or its inverse cannot be expressed as a finite polynomial function of the o(4,2) generators. Therefore no significant simplifications of the problem occur within the o(4,2) framework. It will be seen, however, that the problem can be formulated using *only* the representation theory of o(4,2) if one introduces the following operator replacements [8]:

$$r\rightarrow 2\exp(-\beta)t_3(\beta) \ , \tag{2}$$

$$\mathbf{r}\rightarrow -2\exp(-\beta)\mathbf{a}(\beta) \ , \tag{3}$$

$$\mathbf{p}\rightarrow \exp(\beta)t_3^{-1}(\beta)\mathbf{g}/2 \ , \tag{4}$$

$$p^2\rightarrow \exp(2\beta)[t_3^{-1}(\beta)t_1(\beta)+1]/2 \ . \tag{5}$$

These replacements are approximations which become exact if the limit β going to $+\infty$ is taken at the end of the calculations. The particular case $\beta=0$ was considered in Ref. [8]. In that particular case, the operator replacements were shown to be valid in the limit of highly excited hydrogenic states. The present operator replacements [Eqs. (2)–(5)] allow one to consider not only highly excited states but all states. The Schrödinger equation, Eq. (1), is transformed into Eq. (6) according to the replacements given by Eqs. (2), (3), and (5):

$$[T(\beta)+2(1+\exp(-\beta)\{-[Z/t_3(\beta)]-[Z/t_3'(\beta)]+1/A(\beta)\})-4\exp(-2\beta)E(\beta)][t_3(\beta)t_3'(\beta)]^{1/2}|\Psi(\beta)\rangle=0\ , \tag{6}$$

$$T(\beta)\equiv[t_3(\beta)]^{-1/2}t_1(\beta)[t_3(\beta)]^{-1/2}+[t_3'(\beta)]^{-1/2}t_1'(\beta)[t_3'(\beta)]^{-1/2}\ , \tag{7}$$

$$A(\beta)\equiv|\mathbf{a}(\beta)-\mathbf{a}'(\beta)|\ . \tag{8}$$

$E(\beta)$ and $|\Psi(\beta)\rangle$ denote the eigenvalues and eigenvectors, respectively. $T(\beta)$ is Hermitian. The vector

$$[t_3(\beta)t_3'(\beta)]^{1/2}|\Psi(\beta)\rangle$$

is expanded in an orthonormal basis and one finally obtains a Hermitian matrix for Eq. (6). The expansion concerns the above vector rather than the vector $|\Psi(\beta)\rangle$ because the scalar product of quantum mechanics is obtained from the presently used scalar product if the vectors are premultiplied by $(rr')^{1/2}$ which corresponds, apart from normalization, to the prefactor $[t_3(\beta)t_3'(\beta)]^{1/2}$ within the replacement given by Eq. (2).

The remaining part of this section is devoted to a complete description of the construction of the orthonormal two-electron basis. This material has already been presented elsewhere [10,11,8,12] for the essential part, but is presented once more here for self-consistency. The only new part is the construction of basis vectors that are eigenvectors of the two-electron permutation operator. This part is essential for numerical applications of the method that is described in Sec. III.

The prerequisite starting point is the knowledge of the hydrogenic states $|n,l,m\rangle$. One then constructs scaled hydrogenic states, also called Sturmian states:

$$|(n,l,m)\beta\rangle\equiv n\exp\{i[\beta+\ln(n)]t_2\}|n,l,m\rangle\ . \tag{9}$$

The ket notation $|\ \rangle$ does not include the spin space. The action of the 15 o(4,2) β-dependent generators introduced at the beginning of this paper on the these scaled hydrogenic states is given explicitly in Ref. [5]. The phase conventions of Ref. [5] are maintained in the present paper. From the group-theoretical point of view, the action of these 15 generators corresponds to a unitary irreducible representation of the group O(4,2). The action of these generators is very similar to the action of three generators of the angular momentum algebra: the quantum numbers n,l,m only change by plus or minus unity. It is this fact that leads finally to a sparse matrix in the two-electron problem which is now considered. One first defines eigenstates of the total angular momentum using the SU(2) Clebsch Gordan coefficients:

$$|(n,l,n',l',L,M)\beta\rangle \equiv \sum_{m,m'}\langle l,m;l',m'|LM\rangle|(n,l,m)\beta\rangle|(n',l',m')\beta\rangle\ . \tag{10}$$

L is the quantum number associated with the total orbital angular momentum, M the one associated with its projection on an arbitrary fixed axis. An essential contribution of Refs. [10,11] was to show that a more appropriate basis for the two-electron atomic problem was

$$|(n,n',J_1,J_2,L,M)\beta\rangle\equiv\sum_{l,l'}|(n,l,n',l',L,M)\beta\rangle[(2l+1)(2l'+1)(2J_1+1)(2J_2+1)]^{1/2} \times(-1)^{l'}\begin{Bmatrix}\frac{1}{2}(n-1) & \frac{1}{2}(n'-1) & J_1\\ \frac{1}{2}(n-1) & \frac{1}{2}(n'-1) & J_2\\ l & l' & L\end{Bmatrix}\ . \tag{11}$$

This corresponds to another coupling of the four angular momenta that are present in the two-electron atomic problem. Two of these four angular momenta are linear combinations of the angular momentum of the electron and of the restricted Runge Lenz vector of the same electron. They correspond to an angular momentum quantum number $j=(n-1)/2$. The two others correspond to the same linear combinations, but for the second electron $[j'=(n'-1)/2]$. From a strict viewpoint, each of these four angular momenta is not really an angular momentum. They satisfy the usual commutation relations pertaining to angular momentum algebra but, for example, do not behave like an angular momentum by time reversal. The 9-j symbols in Eq. (11) explicitly show the two different couplings of these four angular momenta: the first column corresponds to the coupling of the pair associated with one electron. This coupling yields the monoelectronic angular momentum l. The second column corresponds to the coupling of the pair associated with the second electron. This coupling yields the monoelectronic angular momentum l'. The first two lines correspond to coupling of the angular momentum referring to different electrons, which results in the introduction of the collective quantum numbers J_1,J_2. The further step is the construction of the eigenstate of the parity operator [11]. An elementary calculation shows that the vectors defined by

$$|(n,n',J_1,J_2,L^{\pi},M)\beta\rangle \equiv \alpha(J_1,J_2)[\,|(n,n',J_1,J_2,L,M)\beta\rangle + \pi(-1)^{n+n'+J_1+J_2+L}|(n,n',J_2,J_1,L,M)\beta\rangle\,] \ , \tag{12}$$

where

$$\alpha(a,b) \equiv \tfrac{1}{2} \ \text{if}\ a=b \ , \ (\tfrac{1}{2})^{1/2} \ \text{otherwise} \ , \tag{13}$$

are normalized eigenvectors of the total parity operator with eigenvalue π. The final step is the construction of eigenvectors of the two-electron permutation operator P. From the easily derived property

$$P|(n,n',J_1,J_2,L,M)\beta\rangle = (-1)^{L}|(n',n,J_2,J_1,L,M)\beta\rangle \ , \tag{14}$$

one finally obtains

$$P|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle = (-1)^{S}|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle \tag{15}$$

where

$$|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle \equiv \alpha(n,n')[\,|(n,n',J_1,J_2,L^{\pi},M)\beta\rangle + (-1)^{L+S}|(n',n,J_2,J_1,L^{\pi},M)\beta\rangle\,] \ . \tag{16}$$

It is recalled that the spin is not included in the present ket notation and therefore the vectors are eigenvectors of the two-electron permutation operator with eigenvalue $+1$ if the total spin characterized by the quantum number S is equal to zero and with eigenvalue -1 if $S=1$. Other useful and easily derived properties of these basis vectors are the following:

$$|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle = \pi(-1)^{n+n'+J_1+J_2+S}|(n',n,J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle \ , \tag{17}$$

$$|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle = \pi(-1)^{n+n'+J_1+J_2+L}|(n,n',J_2,J_1,{}^{2S+1}L^{\pi},M)\beta\rangle \ . \tag{18}$$

It follows in particular that if $J_1=J_2$, then $\pi=(-1)^{L}$, because otherwise the vector is equal to its opposite and therefore equal to the null vector. To summarize, all the vectors defined by Eq. (16) and subject to the restrictions

$$n \geq n', \quad J_1 \geq J_2, \quad J_1 \neq J_2 \ \text{if}\ \pi \neq (-1)^{L} \ ,$$
$$n \neq n' \ \text{if}\ \pi \neq (-1)^{J_1+J_2+S} \tag{19}$$

provide a complete set of linearly independent orthonormal vectors in the subspace characterized by fixed values of L,M,π,S. Otherwise states, they provide an orthonormal basis.

III. THE SYMMETRIC SPARSE MATRIX AND ITS NUMERICAL DIAGONALIZATION

The replaced Schrödinger equation, Eq. (6), involves only o(4,2) generators. The actions of these generators on the monoelectronic states given by Eq. (9) are explicitly known [5]. The two-electron basis vectors given by Eq. (16) have been constructed from the monoelectronic states given by Eq. (9) in Sec. II. The action of the operators involved in the replaced Schrödinger equation, Eq. (6), on the two-electron basis vectors given by Eq. (16) can therefore be deduced. These basis vectors have eigenvalues $1/n+1/n'$ with respect to the action of the operator $1/t_3(\beta)+1/t'_3(\beta)$, and eigenvalues

$$\{2[J_1(J_1+1)+J_2(J_2+1)]-L(L+1)\}^{-1/2}$$

with respect to the action of the operator $1/A(\beta)$ [10,11]. It remains to give the action of the operator $T(\beta)$. The action of $T(\beta)$ can be deduced from Eq. (74) of Ref. [8]. The result is

$$\langle x|T(\beta)|y\rangle = \tfrac{1}{2}[\langle x|T_{+}(\beta)|y\rangle + \langle y|T_{+}(\beta)|x\rangle^{*}] \ , \tag{20}$$

where T_{+} is defined by

$$
\begin{aligned}
&T_{+}(\beta)|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle \\
&\quad =\tfrac{1}{2}\alpha(n,n')[(2J_1+1)(2J_2+1)]^{-1/2} \\
&\qquad \times\{(J_1J_2)^{-1/2}c(L,J_1+J_2)[f_n c(j-J_1,j')c(j-J_2,j')/\alpha(n+1,n')|n+1,J_1-\tfrac{1}{2},J_2-\tfrac{1}{2}\rangle \\
&\qquad\qquad +f_{n'}c(j'-J_2,j)c(j'-J_1,j)/\alpha(n'+1,n)|n'+1,J_1-\tfrac{1}{2},J_2-\tfrac{1}{2}\rangle] \\
&\qquad +[(J_1+1)(J_2+1)]^{-1/2}c(L,J_1+J_2+1) \\
&\qquad\quad \times[f_n c(j',j+J_1+1)c(j',j+J_2+1)/\alpha(n+1,n')|n+1,J_1+\tfrac{1}{2},J_2+\tfrac{1}{2}\rangle \\
&\qquad\qquad +f_{n'}c(j,j'+J_2+1)c(j,j'+J_1+1)/\alpha(n'+1,n)|n'+1,J_1+\tfrac{1}{2},J_2+\tfrac{1}{2}\rangle] \\
&\qquad +[(J_1+1)J_2)]^{-1/2}c(J_1-J_2,L)[\alpha(J_1,J_2)/\alpha(J_1+\tfrac{1}{2},J_2-\tfrac{1}{2})] \\
&\qquad\quad \times[-f_n c(j',j+J_1+1)c(j-J_2,j')/\alpha(n+1,n')|n+1,J_1+\tfrac{1}{2},J_2-\tfrac{1}{2}\rangle \\
&\qquad\qquad +f_{n'}c(j,j'+J_1+1)c(j'-J_2,j)/\alpha(n'+1,n)|n'+1,J_1+\tfrac{1}{2},J_2-\tfrac{1}{2}\rangle] \\
&\qquad +[J_1(J_2+1)]^{-1/2}c(J_2-J_1,L)[\alpha(J_1,J_2)/\alpha(J_1-\tfrac{1}{2},J_2+\tfrac{1}{2})] \\
&\qquad\quad \times[-f_{n'}c(j,j'+J_2+1)c(j'-J_1,j)/\alpha(n'+1,n)|n'+1,J_1-\tfrac{1}{2},J_2+\tfrac{1}{2}\rangle \\
&\qquad\qquad +f_n c(j',j+J_2+1)c(j-J_1,j')/\alpha(n+1,n')|n+1,J_1-\tfrac{1}{2},J_2+\tfrac{1}{2}\rangle]\}\ , \qquad (21)
\end{aligned}
$$

where $c(a,b)\equiv[(b+a+1)(b-a)]^{1/2}$, $j\equiv(n-1)/2$, $j'\equiv(n'-1)/2$, $f_n\equiv[n(n+1)]^{1/2}$, and $\alpha(a,b)$ is defined in Eq. (13).

For notational convenience, only the modified quantum numbers of the vectors of the right-hand side of Eq. (21) have been written; for example:

$$
\begin{aligned}
&|n'+1,J_1-\tfrac{1}{2},J_2-\tfrac{1}{2}\rangle \\
&\qquad \equiv|(n,n'+1,J_1-\tfrac{1}{2},J_2-\tfrac{1}{2},{}^{2S+1}L^{\pi},M)\beta\rangle\ .
\end{aligned}
$$

In order to numerically diagonalize the matrix, one has to consider a finite rather than an infinite matrix. All the values of n,n' smaller than or equal to a maximum value, to be denoted N, are taken into account in the numerical calculations. The order of the matrix, to be denoted $O(N,L,S,\pi)$, is determined automatically by the computer but can also be obtained explicitly. The quadruple summation over J_1,J_2,n,n' subject to the triangular inequalities which are implicit in the 9-j symbols of Eq. (11), to the restrictions given by Eq. (19), and to the condition $n\leq N$, is a purely counting problem which requires care but does not present basic difficulties. The result is given in the Appendix. The solutions $E(\beta)$ of Eq. (6) are plotted in Fig. 1 as a function of $\exp(-2\beta)$ for the first ${}^1P^o$ energy level with $Z=2$. One obtains an equation for independent particles which is exactly solvable if the term involving $A(\beta)$, corresponding to the interelectronic repulsion, is omitted in Eq. (6). The corresponding unperturbed discrete energies are obtained by the same method that is given in Ref. [8] for the case $\beta=0$. These energies, denoted by $E_0(\beta,j,k)$ are

$$E_0(\beta,j,k)=\varepsilon(\beta,j)+\varepsilon(\beta,k)\ , \qquad (22)$$

$$
\begin{aligned}
\varepsilon(\beta,j)\equiv&[\exp(2\beta)/4] \\
&\times(1-\{1+[2Z\exp(-\beta)/j]^2\}^{1/2})\ , \qquad (23)
\end{aligned}
$$

with j,k positive integers. The energy $E_0(\beta,1,2)$ and the difference $d(\beta,1,2)$, defined by

$$d(\beta,j,k)\equiv E(\beta)-E_0(\beta,j,k)\ , \qquad (24)$$

are also plotted in Fig. 1. The difference given by Eq. (24) varies slowly with $\exp(-2\beta)$. Therefore the extrapolation to the case $\exp(-2\beta)=0$ will always be carried out on the difference $d(\beta,j,k)$.

The numerical results for the first ${}^1P^o$, ${}^3P^o$, ${}^3S^e$, ${}^3P^e$

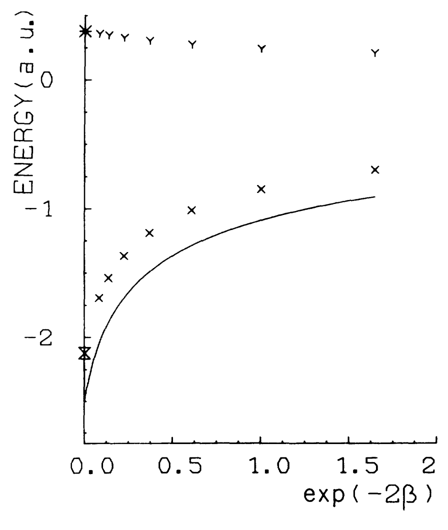

FIG. 1. First ${}^1P^o$ energy level (atomic units) as a function of $\exp(-2\beta)$ for $\beta=-0.25,0.0,0.25,0.5,0.75,1.0,1.25$. Nuclear charge $Z=2$. ×, $E(\beta)$, numerical solutions of Eq. (6). ⧖, solution of the Schrödinger equation from Ref. [14]. Solid line curve, $E_0(\beta,1,2)$. See Eqs. (22) and (23). Y, $d(\beta,1,2)$, the difference between $E(\beta)$ and $E_0(\beta,1,2)$; see Eq. (24). *, ⧖ $-E_0(\infty,1,2)=$ ⧖ $+2.5$.

TABLE I. $E(\beta)$ (in atomic units) as a function of β; T, extrapolated results; V, variational results; A, relative accuracy. It is stressed that the extrapolated results are not obtained directly from the results of this table but by extrapolating $d(\beta,j,k)$ [Eq. (24)] with respect to $\exp(-2\beta)$. For the three first columns, $(j,k)=(1,2)$, for the last one, $(j,k)=(2,2)$.

β	$E(\beta)$			
	State $^1P^o$	$^3P^o$	$^3S^e$	$^3P^e$
−0.25	−0.697 835	−0.698 082	−0.730 840	−0.349 075
0.0	−0.846 143	−0.846 632	−0.882 980	−0.408 799
0.25	−1.011 44	−1.012 35	−1.051 91	−0.469 063
0.5	−1.188 40	−1.189 98	−1.232 12	−0.526 153
0.75	−1.368 52	−1.371 05	−1.414 94	−0.576 440
1.0	−1.540 97	−1.544 72	−1.589 44	−0.617 428
1.25	−1.694 89	−1.700 07	−1.744 76	−0.648 417
1.5			−1.873 04	−0.670 364
T	−2.122 83	−2.132 31	−2.175 13	−0.710 513
V	−2.123 843[a]	−2.133 164[a]	−2.175 229[a]	−0.710 499 5[b]
A	-4.8×10^{-4}	-4.0×10^{-4}	-4.8×10^{-5}	1.9×10^{-5}

[a] Reference [14].
[b] Reference [15].

energy-level solutions of Eq. (6) for $Z=2$ are reported in Table I. As usual, o is for odd parity ($\pi=-1$), and e for even parity ($\pi=1$). It has been noted [7,8] that the operator replacement for the interelectronic interaction is not possible for $L=0$ since the eigenvalues of A is then zero for the case $n=n'$, $J_1=J_2=0$, and therefore A has no inverse. However, this case is excluded for triplet states with $L=0$. As a result, the present method applies for triplet but not for singlet $L=0$ states. The size of the truncated basis (equivalently, the order of the matrix) increases rapidly with the N maximum value of n,n'. The number N for which convergence can be achieved increases with β. Thus, for the $^1P^o$, $^3P^o$ energy levels, six digits for $E(\beta)$ do not change when N moves between 17 and 30 for the case $\beta=0$. In both cases, the order of the corresponding matrices is 1632 if $N=17$, 8990 if $N=30$. For $\beta=1.25$, convergence is obtained for $N=35$ and the order is 14 280 for both energy levels $^1P^o$, $^3P^o$. For the $^3S^e$, $^3P^e$ energy levels, the size of the truncated bases for fixed N is smaller. The calculations have therefore been performed up to $\beta=1.5$, and convergence was obtained for $N=45$. This corresponds to matrices of order 15 180 for both energy levels $^3S^e$, $^3P^e$. The algorithm used for numerical determination of the eigenvalues of sparse matrices is iterative [13]. The extrapolation with respect to $\exp(-2\beta)$ to the limiting case of infinite β was made using a Lagrange interpolating polynomial. The accuracy of the present final results (last line of Table I) is essentially limited by this extrapolation. These extrapolated results are tested by comparison with variational results from Refs. [14,15].

IV. CONCLUDING REMARKS

The disadvantages pertaining to the extrapolation with respect to $\exp(-2\beta)$ have some counterparts. Firstly, the mathematical properties of the solutions of Eq. (6) for fixed β should be easier to study than those of the Schrödinger equation for two-electron atoms. For example, the operator $1/t_3(\beta)$ is bounded whereas $1/r$ is not. This is interesting from the viewpoint of functional analysis. Secondly, the only nondiagonal elements of the matrices associated with Eq. (6) are the ones of the operator $T(\beta)$ which originates from the kinetic-energy terms. In particular, the fact that the matrix of $1/A(\beta)$, corresponding to the interelectronic potential, is diagonal and extremely simple is a major advantage when compared to the complexity of the two-electron integrals in standard methods.

Only a few bound states, i.e., discrete eigenvalues of Eq. (6), have been presently considered. They all correspond to the situation where the degrees of excitation of the two electrons are quite comparable. For other situations, a generalization of the method by introducing two dimensionless parameters β,β' rather than only one would be appropriate in order that the convergence of the results with respect to the size of the truncated basis be more rapid.

We hope that the present method can also be used in the study of autoionizing states. One way to implement the method of complex coordinates within the present approach would be the addition of a negative imaginary part to β. It is, however, more difficult to study numerically a symmetric complex matrix than a Hermitian matrix. The fact that only diagonal elements become complex will perhaps simplify this numerical problem.

ACKNOWLEDGMENT

The author thanks Mrs. Auby for her kind assistance in numerical computations.

APPENDIX

Two cases have to be distinguished for the explicit expression of the order $O(N,L,S,\pi)$ (see Sec. III) of the matrix. If L is even

$$\begin{aligned}O(N,L,S,\pi)=&-\tfrac{1}{8}\{[1-\pi(-1)^S](1+\pi)(N-\tfrac{1}{2}L)(N+1-\tfrac{1}{2}L)\}-L[(L+2)(L+4)/12+(N-L-1)(N+1-\tfrac{1}{2}L)]/4\\&+\tfrac{1}{2}\pi\{(N-L-1)(N-L)[(N-L+1)/6+\tfrac{1}{2}(L+1)]+(\tfrac{1}{2}L+1)[N(\tfrac{1}{2}L+1)-L(5L+11)/12]\}\\&+[N(N+1)^2(N+2)-(L+1)(L+2)^2(L+3)]/24\\&-(N-L-1)(N-L)[(N-L-1)(N-L)+4N-4L+2]/24\\&-(N-L-1)L(L+1)(L+2)/12+(L+2)(L+4)(L^2+6L+6)/96\;.\end{aligned}\tag{A1}$$

If L is odd

$$\begin{aligned}O(N,L,S,\pi)=&-\tfrac{1}{8}([1-\pi(-1)^S](1-\pi)[N-\tfrac{1}{2}(L+1)][N+1-\tfrac{1}{2}(L+1)]\\&+[1-\pi(-1)^S](L-1)\{(L+1)(L+3)/12+(N-L-1)[N-\tfrac{1}{2}(L-1)]\}\\&+[1+\pi(-1)^S](L+1)\{(L+3)(L+5)/12+(N-L-1)[N-\tfrac{1}{2}(L-3)]\})\\&-\tfrac{1}{2}\pi((N-L-1)(N-L)\{(N-L+1)/6+[1+\tfrac{1}{2}(L-1)]\}+(L+1)(L+3)(6N-5L-1)/24)\\&+[N(N+1)^2(N+2)-(L+1)(L+2)^2(L+3)]/24\\&-(N-L-1)(N-L)[(N-L-1)(N-L)+4N-4L+2]/24\\&-(N-L-1)L(L+1)(L+2)/12+(L+1)(L+3)^2(L+5)/96.\end{aligned}\tag{A2}$$

The terms involving N to the fourth power are equal and opposite sign and therefore the order of the matrix varies as N to the third power. For the case $L=0$, $S=1$, $\pi=1$ and for the case $L=1$, $S=1$, $\pi=1$ the above general expressions take a particular simple form:

$$O(N,L=0\text{ or }L=1,S=1,\pi=1)=(N-1)N(N+1)/6\;.\tag{A3}$$

---

[1] D. Delande and J. Gay, Phys. Rev. Lett. **57**, 2006 (1986).

[2] D. Wintgen and H. Friedrich, Phys. Rev. Lett. **57**, 571 (1986).

[3] D. Delande, A. Bommier, and J. C. Gay, Phys. Rev. Lett. **66**, 141 (1991).

[4] Chun-ho Iu, George R. Welch, Michael M. Kash, Daniel Kleppner, D. Delande, and J. C. Gay, Phys. Rev. Lett. **66**, 145 (1991).

[5] B. G. Adams, J. Cizek, and J. Paldus, Adv. Quantum Chem. **19**, 1 (1988).

[6] E. U. Condon and H. Odabasi, *Atomic Structure* (Cambridge University Press, London, 1980).

[7] E. de Prunelé, J. Math. Phys. **30**, 2891 (1989).

[8] E. de Prunelé, Phys. Rev. A **41**, 2322 (1990).

[9] A. O. Barut and G. L. Bornzin, J. Math. Phys. **12**, 841 (1971).

[10] C. Wulfman, Chem. Phys. Lett. **23**, 370 (1973).

[11] O. Sinanoglu and D. R. Herrick, J. Chem. Phys. **62**, 886 (1975).

[12] E. de Prunelé, Phys. Rev. A **44**, 90 (1991).

[13] We use the subroutine F02FJF of the NAG library. *Fortran Library Manual, Mark 13* (The Numerical Algorithms Group Ltd., Oxford, 1989). This subroutine computes eigenvalues from the largest one in absolute value. We therefore shift our original matrix by a negative multiple of the identity.

[14] Y. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A **4**, 516 (1971).

[15] G. W. F. Drake and A. Dalgarno, Phys. Rev. A **1**, 1325 (1970).