

APPLICATION OF A MODIFIED INTERELECTRONIC POTENTIAL TO THE CALCULATION OF THE ENERGY OF SOME HELIUM S STATES

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Model potentials constructed from selected terms of the multipolar expansion of the interelectronic potentials are defined and applied to the calculation of the 1^1S , 2^1S and 3^1S states of the helium atom. The convergence of the energies as a function of the number of multipole terms in the potential is discussed. The convergence patterns of the configuration interaction expansions in the case of a given potential are studied.

1. Introduction

The great complexity in the ab initio procedures limits the applicability of all but a few methods to small atoms. Thus simplified methods are desirable for many applications. Among these an important role play the methods based on the use of model potentials, effective potentials and pseudopotentials. For surveys of the rich literature in this field we will refer to the recent papers of Durand and Barthelat [1], and Dalgaard and Linderberg [2]. An interesting model approach, which consists in the modification of the interelectronic repulsion term has been proposed by Callan [3].

In the present note we would like to consider a model Hamiltonian for atomic systems which also involves a modification of the potential, viz. the interelectronic potential is replaced by a model potential constructed from selected terms of the multipolar expansion of the standard potential. This potential allows for a considerable reduction of the computational effort involved in the evaluation of the matrix elements of the Hamiltonian. This is due to the fact that in the course of evaluation of the most cumbersome integrals comprising the inverse of the interelectronic distance one has not to consider infinite summations and therefore the variety of radial integrals involved in the computation is strongly reduced. The latter fact simplifies both their generation and storage.

There exist intimate relations between the present approach and the standard methods of atomic structure calculations based on the use of selected configurations of one-electron

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tronic states of definite angular symmetry, e. g. the configuration interaction (CI) method. We discuss this problem in the following section. In order to shed some light on properties of the model potential we present the energies obtained for ground state and two excited states of the helium atom.

2. The model Hamiltonian

We shall assume that the Hamiltonian for an N electron atom may be written in the form

$$H^\Omega = \sum_{i=1}^N h_i + \sum_{i<j}^N v_{ij}^\Omega, \quad (1)$$

where

$$h_i = -\frac{1}{2} \Delta_i + \frac{Z}{r_i}. \quad (2)$$

The repulsion potential for a pair of electrons is defined as

$$v_{ij}^\Omega = \sum_{k \in \Omega} (r_{<}^k / r_{>}^{k+1}) (C^{(k)}(i) C^{(k)}(j)) \quad (3)$$

where Ω represents the set of k values involved in the summation, and $r_{<}$ is the lesser and $r_{>}$ the greater of r_i and r_j . The tensor operators of rank k , $C_p^{(k)}(i)$, are defined in terms of the spherical harmonics [4]. The paranthesis denotes the scalar product. This expression represents a selection of terms of the well known Laplace expansion of the interelectronic repulsion operator, i. e.

$$\bar{v}_{ij}^\Omega = 1/r_{ij}, \quad (4)$$

where $\bar{\Omega}$ denotes the set of all nonnegative integers, and r_{ij} stands for the distance between the electrons i and j . Because the individual terms in (3) are Hermitian operators, the operator H^Ω is Hermitian. We shall denote by E^Ω the eigenvalues of H^Ω .

There exist close connections between the method based on the use of the Hamiltonian (1) and the standard approach in the case when the wavefunction is approximated by a superposition of selected configurations of one-electronic functions. It may be easily shown that for every choice of the configurations there exists a model potential of the type defined in Eq. (3) which leads to results identical with those obtained for the exact interelectronic potential. The minimum set, Ω_{CI} , is determined by the angular structure of the atomic orbitals employed for the construction of the many-electron basis functions (configurations). For example, if only s and p orbitals are involved, the minimum set is $\Omega_{\text{CI}} = \{0, 1, 2\}$. It should be noted that the results of the CI method are upper bounds to the eigenvalues of both the exact Hamiltonian $H = H^{\bar{\Omega}}$ and $H^{\Omega_{\text{CI}}}$.

The main difference between the two methods consists in the fact that instead of restricting the number of configurations used for approximating the wavefunction we

restrict the number of multipole terms in the interelectronic potential. In the former approach one is usually interested in the convergence of the results as a function of the types of angular terms in the wavefunction whereas in our case we investigate the convergence as a function of the number of multipole terms in the model potential.

3. Application to the helium atom S -states

3.1. Method of calculation

For S states of two-electron systems the space part of the exact wavefunction of the i -th state may be written in the " l -expansion" form [5, 6]

$$\Psi_i(1,2) = \sum_{l=0}^{\infty} \Psi_{l,i}(r_1, r_2) P_l(\cos \theta), \quad (5)$$

where θ is the angle between the position vectors of the electrons.

We have performed variational calculations for the model Hamiltonian using the CI method. The approximate function may be written as

$$\Phi_i^{(\bar{l})}(1,2) = \sum_{l=0}^{\bar{l}} \Phi_{l,i}^{(\bar{l})}(r_1, r_2) P_l(\cos \theta). \quad (6)$$

The radial parts of the function (6) are expressed in terms of the exponential basis functions as

$$\Phi_{l,i}^{(\bar{l})} = \sum_{m,n} c_{lmn}^{(\bar{l},i)} (e^{-\eta_1 m r_1} e^{-\eta_1 n r_2} + e^{-\eta_1 n r_1} e^{-\eta_1 m r_2}) r_1^l r_2^l \quad (7)$$

where $c_{lmn}^{(\bar{l},i)}$ are linear variational parameters. The effectiveness of these exponential basis functions has been demonstrated by Jacobs [6] and the present authors [7]. The structure of the basis of the radial functions is similar to that described in [7]. The η values for $l = 4, 5$ have been obtained by extrapolating the optimal results for lower l 's obtained in the latter paper. Special attention was payed to the assessment of the loss of numerical significance caused by a possible approximate linear dependence. For all the expansions discussed in the present work the energies turned out to be stable at least with the accuracy of eight decimal digits.

3.2. Results and discussion

We have considered the model potential (3) for the sets $\Omega = \{0, 1, 2, \dots, \bar{k}\}$. In order to get an idea about the " l -convergence" [5, 7] of the energies for every \bar{k} we computed the energies for various expansion lengths \bar{l} in (6). The results are collected in Tables I–III for the states 1^1S , 2^1S and 3^1S , respectively. The numbers u, v, d, \dots in the symbol (us, vp, wd, \dots) denote the number of terms in (7) for $l = 0, 1, 2$, respectively. In the last line of each table we collected the limits to the energies $E_i^{(\bar{l})}$ obtainable for functions of the form (6) in the case of the standard potential ($\bar{k} = \infty$). One can see from the columns of the Tables that for a fixed angular structure of the basis functions the energies do

not change monotonically when \bar{k} increases. There seems to exist a minimum for the case of $\bar{k} = \bar{l}$. This fact causes that, at least in the case of low \bar{k} values ($\bar{k} \neq 0$), the l -expansion energies for $l = \bar{k}$ are closer to the exact results than their counterpart obtained when the standard potential is used (e. g., in the case of the 1^1S state the $\bar{k} = 1$ sp-limit ($\bar{l} = 1$) to E^{∞} is -2.9013949 , whereas the standard ($\bar{k} = \infty$) sp-limit is -2.900520).

The results displayed in the Tables I–III allow one to get an idea about the l -convergence of the energies for a given model potential ($\bar{k} = \text{const}$). The convergence for low \bar{k} values is rather fast. This is confirmed by our extensive computations for $\bar{k} = 1$ and $\bar{k} = 2$. In this case we obtained the energies of the ground and excited states for all the subsets of the basis sets (5s, 36p, 28d, 21f, 15g, 10h) characterized by increasing \bar{l} values. It turned out that for $\bar{k} = 1$ and $\bar{k} = 2$ the results practically reached their

TABLE I
Variational $E^{(\bar{k})}$ energies for the 1^1S state of He

\bar{k}	Basis sets			
	45s	(45s, 36p)	(45s, 36p, 28d)	(45s, 36p, 28d, 15f)
0	-2.8790237	-2.8790237	-2.8790237	-2.8790237
1	-2.8790237	-2.9013949	-2.9014488	-2.9014488
2	-2.8790237	-2.9005071	-2.9030437	-2.9030637
3	-2.8790237	-2.9005071	-2.9027743	-2.9034013
4	-2.8790237	-2.9005071	-2.9027513	-2.9033001
5	-2.8790237	-2.9005071	-2.9027513	-2.9032864
6	-2.8790237	-2.9005071	-2.9027513	-2.9032843
∞	-2.879028*	-2.900520*	-2.902774*	-2.903307*

* Extrapolated results of Bunge [5].

TABLE II
Variational $E^{(k)}$ energies for the 2^1S state of He

k	Basis sets			
	45s	(45s, 36p)	(45s, 36p, 28d)	(45s, 36p, 28d, 15f)
0	-2.14419299	-2.1441930	-2.1441930	-2.1441930
1	-2.14419299	-2.1458138	-2.1458170	-2.1458170
2	-2.14419299	-2.1457622	-2.1459267	-2.1459279
3	-2.14419299	-2.1457622	-2.1459108	-2.1459496
4	-2.14419299	-2.1457622	-2.1459094	-2.1459437
5	-2.14419299	-2.1457622	-2.1459094	-2.1459429
6	-2.14419299	-2.1457622	-2.1459094	-2.1459428
∞	-2.144197*	-2.145766*	-2.145914*	-2.145948*

* Extrapolated results of Jankowski et al. [7].

TABLE III

Variational $E(\bar{k})$ energies for the 3^1S state of He

k_{\max}	Basis sets			
	55s	(55s, 36p)	(55s, 36p, 21d)	(55s, 36p, 21d, 10f)
0	-2.0607912	-2.0607912	-2.0607912	-2.0607912
1	-2.0607912	-2.0612260	-2.0612269	-2.0612269
2	-2.0607912	-2.0612115	-2.0612567	-2.0612571
3	-2.0607912	-2.0612115	-2.0612522	-2.0612627
4	-2.0607912	-2.0612115	-2.0612519	-2.0612612
5	-2.0607912	-2.0612115	-2.0612519	-2.0612610
6	-2.0607912	-2.0612115	-2.0612519	-2.0612610
∞	-2.060794*	-2.061215*	-2.061256*	-2.061265*

* Extrapolated results of Jankowski et al. [7].

TABLE IV

Estimates of the eigenvalues of the model Hamiltonian for low \bar{k} values

\bar{k}	1^1S		2^1S		3^1S	
	Energy	Percentage of E_∞	Energy	Percentage of E_∞	Energy	Percentage of E_∞
0	-2.879028	99.150	-2.144197	99.917	-2.060794	99.977
1	-2.901453	99.922	-2.145821	99.993	-2.061230	99.998
2	-2.903068	99.978	-2.145932	99.998	-2.061260	99.999
∞	-2.903724*		-2.145974**		-2.061272**	

* Perkins [8]. ** Winkler and Porter [9].

lower bounds for $\bar{l} = 2$ and $\bar{l} = 3$ respectively. The energies E^{Ω} obtained for the full basis set are displayed in Table IV. It seems that they differ from their exact counterparts at most by $5 \cdot 10^{-6}$.

The energies E^{Ω} (for $\bar{k} \neq 0$) are very close to the exact values obtained with the full interelectronic potential ($\bar{k} = \infty$). This is already true for the $\bar{k} = 1$ results. The largest difference is disclosed for the ground state. But even in this case one obtains 99.92% of the total energy or 95% of the correlation energy. The results for both the excited states are considerably closer to the exact eigenvalues of the standard Hamiltonian than for the ground states. In this case even the pure radial potential ($\bar{k} = 0$) allows us to approach the standard results within the accuracy just mentioned for the ground state.

4. Conclusions

The results obtained for the helium atom indicate that only a few terms of the multipolar expansion of the exact interelectronic potential are essential in the computations of the energy of atomic systems. For the S states only the two first terms, $\bar{k} = 0, 1$,

are necessary to obtain accuracies within the range 99.922–99.998%. We expect that the same is true for other properties except perhaps the expectation values of r_{12}^{-1} and $\delta(r_{12})$. In the case of our model potentials the CI method proved to be very fast convergent. It turned out that the CI expansion may be limited to $\bar{l} = \bar{k} + 1$ (or even $\bar{l} = \bar{k}$).

Before proceeding to applications of the modified potentials to larger atomic systems more attention should be paid to the problem of the optimal choice of Ω for systems comprising p, d or f electrons. In this case the number of term in Eq. (3) certainly increases in comparison with the helium atom. However, the analysis of the existing CI results for larger atoms indicate that it should be possible to define useful model potentials comprising only a few multipolar terms.

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