

CALCULATIONS IN A MODEL POTENTIAL FIELD FOR THE ISOELECTRONIC SERIES OF THE Li ATOM

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The pseudopotential method is used to calculate the ground states and excited states of the Li atom and those of the ions of its isoelectronic series in the first row of the periodic system. The energy eigenvalues and the pseudowavefunctions were computed numerically. The agreement between the calculated and empirical energies is good. The method is appropriate to consider the effect of the inner orbitals of many-electronic systems on the valency electrons.

Introduction

The solution of the Hartree—Fock equations causes great difficulties in the computations of atomic, molecular and solid state properties. There are a number of attempts to simplify either the methods of solution or the structure of the equations. One of the possibilities is the introduction of the pseudopotentials, which means to take into account the orthogonality of the valence states to the core states with a repulsive term [1]. In the Hartree—Fock equations one may try to substitute the sum of the terms of the nucleus-electron interaction, the Coulomb and the exchange-interaction with a Coulomb like and a non-local repulsive potential. In this way we can attain so considerable a reduction on the computational effort that the calculations may be carried out for the atomic systems with small or medium size computers [2]. There are further possibilities of the applications of this method in the molecular and the solid state field.

We have tried to substitute the non local potential with a linear combination of a local radial part multiplied by projection operators in the angular momentum space. The local radial part is a Gauss-type term, which contains some adjustable parameters. The values of these parameters have been obtained numerically with a semiempirical procedure. Substituting these values of parameters into the Gaussian term, we have calculated some energy eigenvalues and pseudowavefunctions of the Li atom and its isoelectronic series, numerically too.

The pseudopotential

Let us consider the Hartree–Fock equations of an atom with N electrons in the form

$$\left[H(1) + \sum_{j=1}^N \langle \psi_j | r_{12}^{-1} (1 - P_{12}) | \psi_j \rangle \right] \psi_i(1) = E_i \psi_i(1), \quad (1)$$

where

$$H(1) = -\frac{1}{2} \Delta_1 - \frac{z}{r_1}, \quad (2)$$

z the atomic number, P_{12} the permutation operator and the quantities are measured in atomic units.

If we use the Eq. (1) the wavefunction of the atom is

$$\psi = N^{-\frac{1}{2}} \begin{vmatrix} \psi_1(1) & \psi_1(2) & \dots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & \dots & \psi_2(N) \\ \dots & \dots & \dots & \dots \\ \psi_N(1) & \psi_N(2) & \dots & \psi_N(N) \end{vmatrix}, \quad (3)$$

where ψ_N is the wavefunction of the valence electron and the ψ_i functions are assumed to be orthogonal ones. Let us write ψ_N in the following form:

$$\psi_N = \psi_0 - \sum_{i=1}^{N-1} c_i \psi_i, \quad c_i = \langle \psi_i | \psi_0 \rangle, \quad (4)$$

where ψ_0 is *not* orthogonal to the core functions ψ_i . We can substitute (4) into the determinant (3), and we get the Hartree–Fock equations (1) in the form

$$(H_F + V_R) \psi_0 = E_N \psi_0, \quad (5)$$

where

$$H_F = H(1) + \sum_{j=1}^{N-1} \langle \psi_j | r_{12}^{-1} (1 - P_{12}) | \psi_j \rangle, \quad (6)$$

and

$$V_R = \sum_{j=1}^{N-1} (E_N - E_j) | \psi_j \rangle \langle \psi_j |. \quad (7)$$

V_R is called the pseudopotential.

HELLMANN suggested [3] that the total interaction potential should be written in the form

$$V_H = -\frac{Z}{r} + A \exp \{-ar\} / r. \quad (8)$$

We can discover other forms such as $-Z/r + A e/r^{-ar}$, $-Z/r + A e/r^{-r^2}$ and so on used before. The latter form has been employed by RAY and SWITALSKI [4].

With this potential we have also calculated numerically some energy eigenvalues and the eigenfunctions using the parameters obtained by RAY and SWITALSKI.

Let the form of the pseudopotential be

$$V(r) = -\frac{Z}{r} + \sum_l A_l e^{-a_l r^2} P_l, \quad (9)$$

where Z is the nuclear charge minus the number of core electrons and A_l and a_l the parameters of the pseudopotential for the state with quantum number l , respectively, P_l projection operator. The potential consists of two terms: the first is a Coulombic term and the second has Gaussian form. The latter will be used for the description of an electron, moving in the field of an $(1s)^2$ closed shell ion excluding the Coulomb term, but including all other interactions e.g. correlation, polarization, etc.

There are a number of ways to determine the parameters of (9). At the first trial a variational method with doublezeta wave functions has been used. The computed energy-values were fitted to the $2s$, $3s$ and $2p$, $3p$ terms of the Li atom and the ions of its isoelectronic series, resp. [5].

Here the parameters A_l and a_l have been determined by a numerical procedure. Let us consider the one-electron wavefunctions in the form

$$\psi_{nlm}(r, \vartheta, \chi) = \frac{1}{r} P_{nl}(r) Y_{lm}(\vartheta, \chi), \quad (10)$$

where Y_{lm} are spherical harmonics. Because the computations have been carried out for atoms containing one valency electron, the dependence of one-electron wavefunctions upon the spin coordinates has been neglected.

By inserting the function (10) into the equation

$$\left[-\frac{1}{2} \Delta_{r\vartheta\chi} + V(r) \right] \psi_{nlm} = E_{nl} \psi_{nlm} \quad (11)$$

obtained from the Eqs. (5) and (6), and multiplying the Eq. (11) from left by the $\langle Y_{lm} |$, we obtain the radial Schrödinger equation

$$\frac{1}{2} \frac{d^2 P_{nl}}{dr^2} + \left(E_{nl} - \frac{l(l+1)}{r^2} - V_l(r) \right) P_{nl} = 0. \quad (12)$$

To simplify the form of Eq. (12), it is convenient to introduce Rydberg units for the energy and the potential. Then Eq. (12) becomes

$$\frac{d^2 P_{nl}}{dr^2} + \left(E_{nl} - \frac{2l(l+1)}{r^2} - 2V_l(r) \right) P_{nl} = 0. \quad (13)$$

The numerical solution of this equation has been obtained by a subroutine suggested by HERMAN and SKILLMAN [6]. The potential $V_l(r)$ in Eq. (13) has to satisfy the conditions

$$\lim_{r \rightarrow 0} rV_l(r) = -Z \quad (14a)$$

and

$$\lim_{r \rightarrow \infty} V_l(r) = 0, \quad (14b)$$

which is in agreement with the form (9) selected by us. The parameters A_l and a_l in (9) have been determined by the requirement that the energy value for the ground state and the energy value for the first excited state (if $l = 0$), the energy values of the first and second excited states (if $l = 1$) computed from (13) agree with the experimental values, respectively. This requirement means that we have to solve the equations

$$E_{n_l}^c(A_l, a_l) = E_{n_l}^{\text{exp}}, \quad n = n_1, n_2, \quad (15)$$

where $E_{n_l}^c(A_l, a_l)$ are the computed energy values at some parameter values and $E_{n_l}^{\text{exp}}$ is the experimental value.

The solution of the system of equations (15) has been obtained by determining the roots of the nonlinear equation

$$f(A_l, a_l) = \left| \frac{E_{n_l}^c(A_l, a_l) - E_{n_l}^{\text{exp}}}{E_{n_l}^{\text{exp}}} \right| + \left| \frac{E_{n_2}^c(A_l, a_l) - E_{n_2}^{\text{exp}}}{E_{n_2}^{\text{exp}}} \right|. \quad (16)$$

The Gauss—Seidel method and/or a random-search method has been suitable for this purpose. The convergence of both methods has been nearly the same.

The function $f(A_l, a_l)$ in Eq. (16) has been regarded to be zero, if the $|f| < \varepsilon$ condition has been satisfied, where $\varepsilon = 0.01$ has been selected in our case.

Discussion of results

The calculations with the Gaussian pseudopotential (9) were performed on the Li atom and the ions of its isoelectronic series. The parameters have been determined for the $l = 0$ and $l = 1$ states. The reference energy levels have been the lowest experimental states $2s$, $3s$ and $2p$, $3p$, respectively.

In Table I the parameter values determined with the double-zeta wavefunction and the numerical one are presented. We may observe considerable agreement between the parameters a_l , computed with different wavefunctions. In the calculational process more roots of function (16) have been obtained at some elements. In this case the values lying nearest to the values obtained by the double-zeta wavefunction method have been chosen.

Table Ia

Parameters of the potential $V_l(r)$ determined with the double-zeta wavefunction variationally and with the numerical method ($l = 0$)

Z	A_0		a_0	
	Double zeta	Numerical	Double zeta	Numerical
1	11.470	53.528	3.1113	3.0881
2	20.345	77.185	5.2933	5.2939
3	30.408	32.178	7.7567	5.2173
4	31.690	52.458	8.0076	8.0076
5	39.390	55.590	9.6892	9.6891
6	54.942	76.330	13.318	13.320
7	78.083	123.12	18.813	18.810

Table Ib

Parameters of the potential $V_l(r)$ determined with the double-zeta wavefunction and with the numerical method ($l = 1$)

Z	A_1		a_1	
	Double zeta	Numerical	Double zeta	Numerical
1	— 5.2287	— 1.0831	1.4464	1.4464
2	— 8.2100	— 8.2080	7.0004	7.0110
3	—11.894	—11.894	13.504	13.504
4	—15.271	—15.083	20.631	20.631
5	—16.603	—16.604	29.156	29.156
6	—17.090	—20.490	37.860	37.860
7	—17.522	—17.980	47.228	47.090

Table IIa

Energy eigenvalues computed by numerical integration for the Li atom at $l = 0$ with different pseudopotentials

n	$-E$ (in Rydberg units) $Z = 1$			
	Experimental	Numerical $A = 53.5287$ $a = 3.08811$	Double zeta $A = 11.47005$ $a = 3.11307$	RAY-SWITALSKI
1	0.39643	0.40210	0.48554	0.39894
2	0.14842	0.14806	0.16510	0.15054
3	0.077262	0.076172	0.082517	0.077467
4	0.047293	0.046383	0.049580	0.047064
5	0.031911	0.031131	0.032776	0.031527

In Tables II—III we present the energy eigenvalues computed by the numerical integration procedure outlined before with the pseudopotential field (9) with the numerical and the double-zeta parameter values, respectively, the RAY—SWITALSKI potential and the experimental energy values [7].

Table IIb

Energy eigenvalues computed by numerical integration for the Li atom at $l = 1$ with different pseudopotentials

$-E$ (in Rydberg units)		$Z = 1$		
n	Experimental	Numerical $A = -1.0831$ $a = -1.44637$	Double zeta $A = -5.22868$ $a = 1.44637$	RAY—SWITALSKI
2	0.26056	0.26095	0.53752	
3	0.11450	0.11287	0.16369	
4	0.063980	0.062729	0.081915	
5	0.040783	0.039842	0.048676	
6	0.028253	0.027489	0.032501	

Table IIIa

Energy eigenvalues computed by numerical integration for the O^{5+} ion at $l = 0$ with different pseudopotentials

$-E$ (in Rydberg units)		$Z = 6$		
n	Experimental	Numerical $A = 76.3259$ $a = 13.32$	Double zeta $A = 54.94254$ $a = 13.318322$	RAY—SWITALSKI
1	10.155	10.244	11.283	10.212
2	4.3208	4.2799	4.6143	4.8958
3	2.3822	2.3340	2.4938	2.6383
4	—	1.4745	1.5502	1.6328
5	—	1.0165	1.0563	1.1066

For saving space the Tables contain the energy values for the Li atom and the O^{5+} ion only. The energy eigenvalues computed with the numerical parameters are in agreement with the experimental ones within the precision of the accuracy of the fitting criterion (16) at the excited states, too. The agreement between the energies calculated by the numerical and the experimental parameters is better than the agreement of the energies with the double-zeta parameters; these latter are sometimes even lower than the experimental ones. This fact can be easily explained, when we observe that the potential (9) with the double-zeta parameters is less repulsive, than the potential with the numerical parameters.

Table IIIb

Energy eigenvalues computed by numerical integration for the O^{5+} ion at $l = 1$ with different pseudopotentials

n	$-E$ (in Rydberg units) $Z = 6$			
	Experimental	Numerical $A = -20.4903$ $a = 37.8607$	Double zeta $A = -17.0903$ $a = 37.8607$	RAY—SWITALSKI
2	9.2770	9.3049	9.3563	9.3531
3	4.0831	4.0684	4.0483	4.0404
4	2.2852	2.2588	2.2617	2.2368
5	—	1.4340	1.4255	1.4271
6	—	0.99093	0.98557	0.98158

The radial pseudowavefunctions with the different parameter values in the potential (9), those of the RAY—SWITALSKI potential and the wavefunction for the Li obtained from the Hartree—Fock calculations [8] are exhibited in Figs. 1, 2, 3 and 4. The wavefunctions are plotted for the states $l = 0$ and $l = 1$ respectively and for the Li atom and O^{5+} ion only. In the Figures it may be seen that the maxima of the numerical wavefunctions are always farther from the origin than those computed with the double-zeta parameters by the same method. This is due to the more powerful repulsion of the poten-

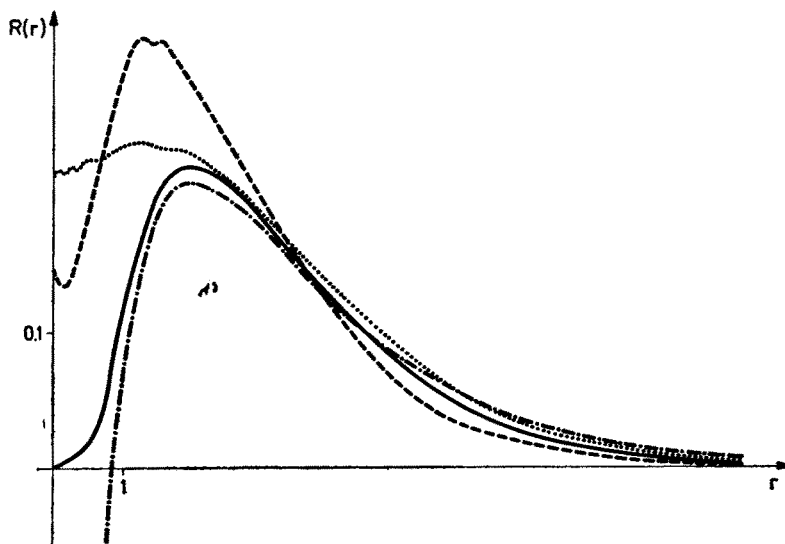


Fig. 1. Radial part of the wavefunctions computed with different parameter sets and different pseudopotentials, and the Hartree—Fock wavefunction for the Li atom at $n = 2$, $l = 0$
 — numerical; - - - double-zeta; . . . RAY—SWITALSKI, - · - · - HARTREE—FOCK

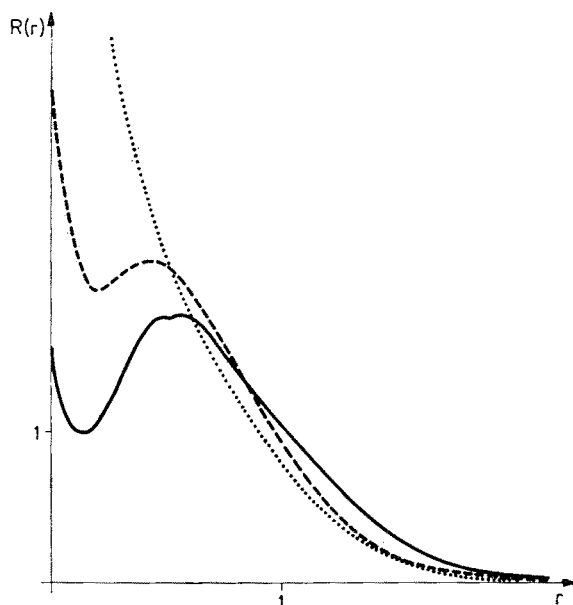


Fig. 2. Radial part of the wavefunctions computed with different parameter sets and different pseudopotentials for the Li atom at $n = 2$, $l = 1$. — numerical; - - - double-zeta; RAY-SWITALSKI

tials obtained by the numerical method, as compared with the other ones. Although the pseudowavefunctions are nodeless (in the ground state) they have some oscillations close to the origin, which is more conspicuous for wavefunctions for the ions with higher atomic number.

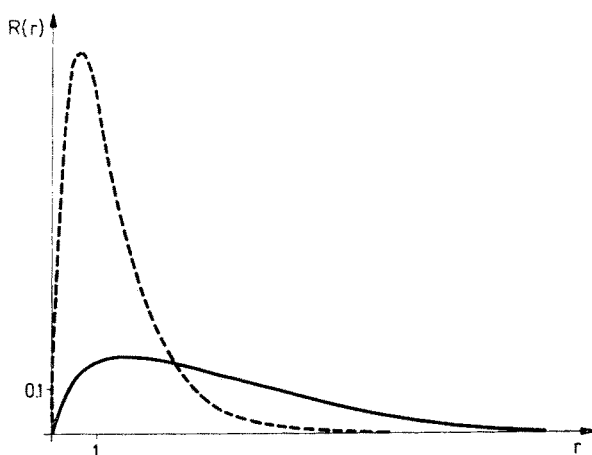


Fig. 3. Radial part of the wavefunctions computed with different parameter sets and different pseudopotentials for the O^{5+} ion at $n = 2$, $l = 0$. — numerical; - - - double-zeta

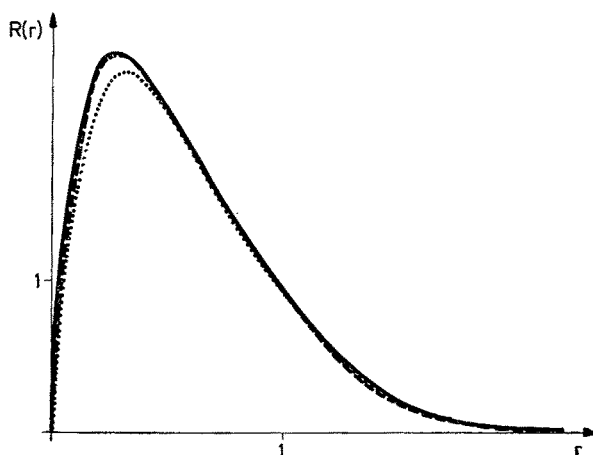


Fig. 4. Radial part of the wavefunctions computed with different parameter sets and different pseudopotentials for the O^{5+} ion at $n=2$, $l=1$. — numerical, - - - double-zeta; . . . RAY—SWITALSKI

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