Calculation of Lower Bounds to Energy Eigenvalues of He, Li^+ and Li by Means of the Effective Field Method

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Two versions of the effective field method have been applied to calculate lower bounds to the energy eigenvalues of the small systems He, Li^+, and Li. Although our modified method leads to an improvement compared with the originally proposed scheme, the results are still far from being satisfying.

1. Introduction

While treatment of atomic and molecular systems be means of variational methods inherently results in upper bounds to the exact energies, the calculation of lower bounds to the eigenvalues of many-electron systems remains a widely unsolved problem.

Methods employed to solve this problem have been reviewed by Reid [1]. Very important are the so-called "intermediate Hamiltonian methods" [2–4]. They have been successfully applied to two electron problems. Another interesting approach is the procedure of Kleindienst [5, 6], which is based on a variational principle. Especially simple from the mathematical point of view is the effective field method (EFM), developed by Hertel, Lieb, and Thirring [7, 8], which has been used to calculate lower bounds to the energy levels of complex atoms.

We were interested in the performance of this method in the case of the ground and lower excited states of relatively small systems like He, Li^+, and Li.

Another point of interest was the question whether the effective field method can be improved in these cases.

2. Computational Method

Within the framework of the effective field method the two-electron part of the Hamiltonian is approximated by a sum of one-electron operators

$$V = \sum_{i=1}^{N-1} \sum_{j>i}^{N} 1/r_{ij} \geqq \sum_{i=1}^{N} \mathrm{P}(r_i) - L, \tag{1}$$

where N is the total number of electrons and $P(r_i)$ an essentially arbitrary potential which only depends on the distance of the i-th electron from the nucleus of the atom. For given $P(r)$, L is a constant depending on $P(r)$ and the electron density $n = -\Delta P(r)/4\pi$ (Δ is the Laplace operator):

$$L = (1/2)\left[\int P(r)\, n(r)\, \mathrm{d}\tau + 3 N^{2/3} \left(\pi \int n(r)^2\, \mathrm{d}\tau\right)^{1/3}\right]. \tag{2}$$

Application of (1) results in a system of one-electron equations

$$-(1/2)\,\Delta u_k - (Z/r)\, u_k + P(r)\, u_k = \varepsilon_k\, u_k \tag{3}$$

which can be solved numerically. The corresponding lower bound is

$$E_{\mathrm{LB}} = \sum_{k=1} n_k\, \varepsilon_k - L, \tag{4}$$

where n_k is the number of electrons with energy ε_k.

The potentials used in this paper and the corresponding expressions for L calculated with (2) are listed in Table 1. Experimental total energies [9] (E_{ex}) of the systems under consideration are given in Table 2.

3. Results and Discussion

The results obtained for He and Li^+ employing potentials P_1 and P_2 are listed in Tables 3 and 4. Comparison of the calculated lower bounds E_{LB1} and E_{LB2} with the experimental ground state energies of He and

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Table 1. Potentials P_i used in this investigation, $1s$ and $2s$ are hydrogen functions with orbital exponents $b/2$ and $b/4$, respectively. For P_1 and P_2 also L_1 and L_2 are given.

$$\begin{aligned}
P_1(r) &= (1-e^{-br})/r \\
L_1 &= (1/4+(3/4)\,N^{2/3})\,b \\
P_2(r) &= \int \frac{1s(2)^2\,\mathrm{d}\tau_2}{r_{12}} = (1-(1+(1/2)\,b\,r)\,e^{-br})/r \\
L_2 &= (5/16+(3/4)\,N^{2/3})\,b/2 \\
P_3(r) &= 2\left((2/3)\int \frac{1s(2)^2\,\mathrm{d}\tau_2}{r_{12}} + (1/3)\int \frac{2s(2)^2\,\mathrm{d}\tau_2}{r_{12}}\right) \\
&= (2-(2/3)(1+(1/2)\,b\,r)\,e^{-br}-(1/3)(1+(3/8)\,b\,r \\
&\quad +(1/16)(b\,r)^2+(1/64)(b\,r)^3)\,e^{-(1/2)br})/r
\end{aligned}$$

Table 2. Experimental total energies [9] of the systems under consideration. All values in a.u.

System	Configuration	Designation	Energy
He	$1s^2$	$1s^2\ {}^1S$	−2.904
	$1s\,2s$	$2s\ {}^3S$	−2.174
	$1s\,2s$	$2s\ {}^1S$	−2.145
Li$^+$	$1s^2$	$1s^2\ {}^1S$	−7.284
	$1s\,2s$	$2s\ {}^3S$	−5.111
	$1s\,2s$	$2s\ {}^1S$	−5.048
Li	$1s^2\,2s$	$2s\ {}^2S$	−7.478
	$1s^2\,3s$	$3s\ {}^2S$	−7.354

Table 3. Lower bounds to the total energies of He and Li$^+$ calculated with potential P_1. E_{LB1} is the value obtained with L_1 calculated according to (2), while $\tilde{E}_{\mathrm{LB1}}$ has been calculated using $\tilde{L}_1$ from (6). The best values are in bold numbers (all energies in a.u.).

	He			Li$^+$		
b	ε_1	E_{LB1}	$\tilde{E}_{\mathrm{LB1}}$	ε_1	E_{LB1}	$\tilde{E}_{\mathrm{LB1}}$
0.25	−1.771	−3.902	−3.792	−4.264	−8.888	−8.778
0.50	−1.581	−**3.882**	−3.662	−4.055	−8.830	−8.610
0.75	−1.421	−3.922	−3.592	−3.870	−**8.820**	−8.490
1.00	−1.287	−4.015	−**3.574**	−3.705	−8.851	−8.410
1.50	−1.080	−4.321	−3.660	−3.426	−9.013	−**8.352**
2.00	−0.934	−4.749	−3.868	−3.202	−9.285	−8.404

Li$^+$ in Table 2 shows that these values are clearly to low.

An improvement can be achieved making use of the relation

$$1/r_{12} \geqq 1/(r_1+r_2) \geqq P(r_1)+P(r_2)-\tilde{L}, \tag{5}$$

from which we obtain $\tilde{L}$ according to

$$\tilde{L} = \mathrm{Max}\,\{P(r_1)+P(r_2)-1/(r_1+r_2)\}. \tag{6}$$

Table 4. Lower bounds to the total energies of He and Li$^+$ calculated with potential P_2. E_{LB2} is the value obtained with L_2 calculated according to (2), while $\tilde{E}_{\mathrm{LB2}}$ has been calculated using $\tilde{L}_2$ from (6). The best values are in bold numbers (all energies in a.u.).

	He			Li$^+$		
b	ε_1	E_{LB2}	$\tilde{E}_{\mathrm{LB2}}$	ε_1	E_{LB2}	$\tilde{E}_{\mathrm{LB2}}$
0.50	−1.755	−3.886	−3.760	−4.252	−8.880	−8.754
0.75	−1.642	−3.848	−3.660	−4.133	−8.830	−8.642
1.00	−1.536	−**3.824**	−3.573	−4.018	−8.788	−8.537
1.50	−1.349	−3.825	−3.449	−3.803	−8.733	−8.357
2.00	−1.194	−3.891	−**3.390**	−3.610	−**8.723**	−8.222
3.00	−0.966	−4.187	−3.434	−3.285	−8.825	−8.072
4.00	−0.820	−4.646	−3.643	−3.033	−9.069	−**8.066**
5.00	−0.728	−5.214	−3.960	−2.838	−9.434	−8.180

Table 5. Lower bounds ($\tilde{E}_{\mathrm{LB2,\,ex}}$) to the total energies of the first excited states of He and Li$^+$ calculated with potential P_2 and L_2 from (6). The best values are in bold numbers (all energies in a.u.).

	He			Li$^+$		
b	ε_1	ε_2	$\tilde{E}_{\mathrm{LB2,\,ex}}$	ε_1	ε_2	$\tilde{E}_{\mathrm{LB2,\,ex}}$
0.50	−1.755	−0.299	−2.304	−4.252	−0.902	−5.404
0.75	−1.642	−0.245	−2.263	−4.133	−0.822	−5.331
1.00	−1.536	−0.213	−**2.250**	−4.018	−0.762	−5.281
1.50	−1.349	−0.184	−2.284	−3.803	−0.685	−**5.239**
2.00	−1.194	−0.172	−2.368	−3.610	−0.644	−5.256
3.00	−0.966	−0.161	−2.629	−3.285	−0.606	−5.393

Table 6. Lower bounds to the total energies of the groundstate ($\tilde{E}_{\mathrm{LB2}}$) and the first excited state ($\tilde{E}_{\mathrm{LB2,\,ex}}$) of Li calculated with potential P_2 and $\tilde{L}_2$ from (9). The best values are in bold numbers (all energies in a.u.).

b	ε_1	ε_2	ε_3	$\tilde{E}_{\mathrm{LB2}}$	$\tilde{E}_{\mathrm{LB2,\,ex}}$
1.00	−4.018	−0.762	−0.283	−9.299	−8.820
1.50	−3.803	−0.685	−0.268	−9.042	−8.625
2.00	−3.610	−0.644	−0.260	−8.866	−8.482
3.00	−3.285	−0.606	−0.251	−8.678	−8.323
4.00	−3.033	−0.588	−0.247	−**8.657**	−**8.316**
5.00	−2.838	−0.576	−0.243	−8.756	−8.423

For P_1 and P_2 we obtained $\tilde{L}_1 = b$ and $\tilde{L}_2 = 0.501\,b$. The corresponding lower bounds ($\tilde{E}_{\mathrm{LB1}}$ and $\tilde{E}_{\mathrm{LB2}}$) are listed together with those from L_1 and L_2 in Tables 3 and 4.

Comparison of the bold entries in Tables 3 and 4 with the corresponding experimental data in Table 2 shows the improvement.

Another choice of the potential P will only lead to a slight further improvement, since the upper bounds

Table 7. Lower bounds to the total energies of the ground-state ($\tilde{E}_{\mathrm{LB3}}$) and the first excited state ($\tilde{E}_{\mathrm{LB3,\,ex}}$) of Li calculated with potential P_3 and $\tilde{L}_3$ from (10). The best values are in bold numbers (all energies in a.u.).

b	ε_1	ε_2	ε_3	$\tilde{E}_{\mathrm{LB3}}$	$\tilde{E}_{\mathrm{LB3,\,ex}}$
1.00	−3.776	−0.571	−0.155	−9.025	−8.609
1.50	−3.451	−0.445	−0.119	−8.701	−8.375
2.00	−3.157	−0.370	−0.101	−8.489	−8.220
3.00	−2.685	−0.285	−0.087	**−8.308**	**−8.110**
4.00	−2.265	−0.239	−0.081	−8.379	−8.221
5.00	−1.957	−0.212	−0.077	−8.638	−8.503

of the energy calculated with the model Hamiltonian

$$H' = -(1/2)\Delta_1 - (1/2)\Delta_2 - Z/r_1 - Z/r_2 + 1/(r_1 + r_2) \tag{7}$$

and the function

$$\psi = 1s(1)\,1s(2) = (\xi^3/\pi)\exp(-\xi r_1 - \xi r_2) \tag{8}$$

are:

$$E'(\mathrm{He}) = -3.24 \text{ a.u.} (\xi = 9/5),$$

$$E'(\mathrm{Li}^+) = -7.84 \text{ a.u.} (\xi = 14/5)$$

(The value of the integral $\langle 1s(1)\,1s(2)|(r_1+r_2)^{-1} \cdot |1s(1)\,1s(2)\rangle$ is $(2/5)\,\xi$). Because we calculated lower bounds of H', which is smaller than the exact Hamiltonian H^{ex}, we cannot get values 'better' than −3.24 and −7.84 a.u. since these values are upper bounds to the corresponding lowest energies of H'.

Use of the potential P_2 and the corresponding $\tilde{L}_2$ shows that the lower bounds to the energies of the lowest triplet and first excited singlet state of both Li$^+$ and He are better than the lower bounds to the corresponding ground state energies (cf. Table 5).

Finally we calculated lower bounds to the energies of Li. With

$$\tilde{L}_2 = \mathrm{Max}\,\{P_2(r_1) + P_2(r_2) + P_2(r_3) - 1/r_{12} - 1/r_{13} - 1/r_{23}\} = 0.501\,b, \tag{9}$$

and

$$\tilde{L}_3 = \mathrm{Max}\,\{P_3(r_1) + P_3(r_2) + P_3(r_3) - 1/r_{12} - 1/r_{13} - 1/r_{23}\} = 0.902\,b \tag{10}$$

we obtained the values given in Tables 6 and 7, respectively.

A comparison of the calculated lower bounds with the experimental energies shows that the EF method even in the presented modified version does not yield acceptable lower bounds to the energy eigenvalues of the systems studied in this investigation.

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