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An exactly soluble base problem for atomic systems

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An exactly soluble base problem for atomic systems is presented which approximates the atomic Hamiltonian as a sum of identical one-electron operators. The eigenfunctions of the one-electron operator consist of a radial function multiplied by a spherical harmonic. Energies for many-electron atoms are found by summing the one-electron energy eigenvalues according to the Pauli principle. These energies are rigorous lower bounds to the exact energies.

The work of Greenlee and Russell [3] provides an exactly soluble base problem for atomic systems using the effective field method of Hertel et al. [1]. However, they obtain this base problem by ignoring the angular momentum operator, thus obtaining only s-state solutions. This note extends their work by including the angular momentum operator. This entails only a minor modification of their procedure and the reader is urged to consult their paper for details.

The atomic Hamiltonian is approximated as a sum of one-electron operators using a modified Coulomb potential. The one-electron problem is

$$-\frac{1}{2r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}\bigl[r\phi(r)\bigr]-\frac{Z}{a}\frac{\mathrm{e}^{-r/a}}{1-\mathrm{e}^{-r/a}}\phi(r)+\frac{1}{2r^2}l(l+1)\phi(r)-\overline{\varepsilon}\phi(r)=0, \qquad (1)$$

where $\overline{\varepsilon} = E + \Lambda$, E is the energy eigenvalue and Λ is a constant given by the effective field theorem. The eigenvalues, E, are then summed according to the Pauli exclusion principle to obtain an approximation to the atomic energy. Greenlee and Russell have shown that this approximation is a rigorous lower bound to the atomic energy – in fact, they constructed the problem so that this would be true.

Exact solutions have not been found for (1) in general. Greenlee and Russell have presented solutions for only the $l = 0$ states. We are able to obtain exact solutions of a slightly different problem for all l states. This problem is

$$-\frac{1}{2r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}\bigl[r\phi(r)\bigr]-\frac{Z}{a}\frac{\mathrm{e}^{-r/a}}{1-\mathrm{e}^{-r/a}}\phi(r)+\frac{1}{2}\frac{\mathrm{e}^{-r/a}}{1-\mathrm{e}^{-r/a}}l(l+1)\phi(r)-\overline{\varepsilon}\phi(r)=0, \qquad (2)$$

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where $\overline{\varepsilon} = E + \Lambda$. We have merely replaced the $1/r^2$ term in the angular momentum operator with $\mathrm{e}^{-r/a}/(1 - \mathrm{e}^{-r/a})$. Since the latter function is everywhere less than the former when a is properly chosen ($a < 1.2$), this problem will also give lower bounds to the atomic energy.

By making the following substitutions:

$$\overline{\phi}(r) = r\phi(r), \qquad x = \frac{r}{a}, \qquad z = \mathrm{e}^{-r/a} = \mathrm{e}^{-x},$$

we obtain

$$z^2 \frac{\mathrm{d}^2}{\mathrm{d}z^2}\overline{\phi} + z\frac{\mathrm{d}}{\mathrm{d}z}\overline{\phi} + 2Za\frac{z}{1-z}\overline{\phi} - l(l+1)a^2\frac{z}{1-z}\overline{\phi} + 2\overline{\varepsilon}\overline{\phi} = 0. \tag{3}$$

We then let

$$\alpha^2 = -2\overline{\varepsilon}a^2 \quad \text{and} \quad \beta^2 = 2Za - l(l+1)a^2.$$

This gives

$$z^2 \frac{\mathrm{d}^2}{\mathrm{d}z^2}\overline{\phi} + z\frac{\mathrm{d}}{\mathrm{d}z}\overline{\phi} + \left(\beta^2\frac{z}{1-z} - \alpha^2\right)\overline{\phi} = 0, \tag{4}$$

which is identical to equation (8) in Greenlee and Russell's treatment. The derivation of the solutions of (4) is given in [3]. Once the solutions to (4) are known, the solutions to (2) are also known. These are

$$\phi_n(r) = \mathrm{e}^{-\alpha r/a}\frac{1 - \mathrm{e}^{-r/a}}{r}\,{}_2F_1\bigl(2\alpha + 1 + n, 1 - n, 2\alpha + 1; \mathrm{e}^{-r/a}\bigr), \tag{5}$$

where n is an integer and ${}_2F_1$ is the hypergeometric series [2] given by

$${}_2F_1(x, y, w, z) = \sum_{k=0}^{\infty} \frac{[x(x+1)\cdots(x+k-1)][y(y+1)\cdots(y+k-1)]}{[w(w+1)\cdots(w+k-1)]}\,\frac{z^k}{k!}$$
$$\text{for } |z| < 1. \tag{6}$$

Note that (6) gives a finite sum if x or y is zero or a negative integer. The radial functions can be coupled to the spherical harmonics for a complete one-electron wavefunction. The eigenvalues are given by

$$\overline{\varepsilon}_n = \frac{-(\beta^2 - n^2)^2}{8a^2n^2} \quad \text{for integer } n < \sqrt{2Za - l(l+1)a^2}. \tag{7}$$

Thus, there are only a finite number of bound states. When the value for β is substituted in (7) we obtain

$$\overline{\varepsilon}_{n,l} = -\frac{Z^2}{2n^2} + \frac{Z}{2a} - \frac{n^2}{8a^2} + \frac{Zal(l+1)}{2n^2} - \frac{a^2l^2(l+1)^2}{8n^2} - \frac{l(l+1)}{4}. \tag{8}$$

The first term is the usual hydrogenic eigenvalue. The second two terms result from Greenlee and Russell's base problem. The final three terms are unique to the base problem presented here. Using the limit on n, one can easily show that the last three terms are a non-negative contribution. Similarly for the second two terms. The constant term Λ is the same for the problem here as in Russell and Greenlee's. They give

$$\Lambda = \frac{Z}{2a}\left[\left(\frac{5}{6}-\frac{\pi^2}{18}\right)+\frac{3}{(2Z)^{2/3}}\left(\frac{1}{6}-\frac{\pi^2}{90}\right)^{1/3}\right]. \tag{9}$$

Combining (8) and (9) gives the one-electron orbital energy as

$$\begin{aligned} E_{n,l} = &-\frac{Z^2}{2n^2}+\frac{Z}{2a}-\frac{n^2}{8a^2}+\frac{Zal(l+1)}{2n^2}-\frac{a^2l^2(l+1)^2}{8n^2}-\frac{l(l+1)}{4} \\ &-\frac{Z}{2a}\left[\left(\frac{5}{6}-\frac{\pi^2}{18}\right)+\frac{3}{(2Z)^{2/3}}\left(\frac{1}{6}-\frac{\pi^2}{90}\right)^{1/3}\right], \end{aligned} \tag{10}$$

where a is a parameter in the modified Coulomb potential.

Table 1 shows the lower bounds obtained from this problem for atoms lithium through neon. These bounds are compared with the lower bounds obtained by Greenlee and Russell and upper bounds presented by them as well. Although the lower bounds have been improved for all atoms with p-electrons, the lower bounds are still far from the upper bounds. Note that our lower bound energies for lithium and beryllium are the same as those of Greenlee and Russell. This is because $l = 0$ for all four orbitals and when $l = 0$, the two problems are equivalent.

The parameter a was chosen to give the highest atomic energy. Since the one-electron problem has only a finite number of bound eigenfunctions, a must be chosen so that the modified Coulomb potential allows for enough orbitals to be filled. In neon, for example, $a = 0.5$ allows for three spatial s-orbitals and three spatial p-orbitals. This gives enough spin-orbitals for the ten electrons of neon. The $3s$-orbital was not used since it has a higher energy than the $2p$-orbital.

Table 1

The previous lower bounds of Greenlee and Russell and upper bounds they reported are compared with the lower bounds of this work. All energies are in Hartree. The parameter a that was used is also given.

Z	Previous lower bound	Lower bound		Upper bound
3	−9.22	−9.22	($a = 0.90$)	−7.43
4	−17.7	−17.7	($a = 0.75$)	−14.6
5	−30.6	−29.3	($a = 0.65$)	−24.5
6	−47.6	−44.7	($a = 0.55$)	−37.7
7	−69.6	−64.3	($a = 0.50$)	−54.3
8	−97.1	−88.5	($a = 0.40$)	−74.8
9	−131	−121	($a = 0.55$)	−99.4
10	−171	−157	($a = 0.50$)	−129

References

[1] P. Hertel, E.H. Lieb and W. Thirring, Lower bounds to the energy levels of complex atoms, J. Chem. Phys. 62 (1975) 3355–3356.

[2] N.N. Lebedev, *Special Functions and Their Applications* (Dover Publications, 1972).

[3] W.M. Russell and D.M. Greenlee, Progress on estimation of energy levels for multi-electron atoms, in: *Numerical Treatment of Eigenvalue Problems*, Vol. 3, International Series of Numerical Mathematics, Vol. 69 (1983) pp. 89–104.