

LETTERS TO THE EDITOR

EVALUATION OF THE ELECTRON AFFINITY OF Li BY USING
AN INTEGRAL IDENTITY FOR THE ENERGY

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The electron affinities (EA) of atoms can be evaluated by the use of the variational principle for energy, by the Glocker's method, and semiempirically. An excellent review of these methods was recently given by Moisewitsch¹. Here we wish to mention that the results of the variational method are strongly dependent on the electron wave functions which are used, and, even with Hartree-Fock wave functions, the correlation and relativistic effects should be included in order to obtain a reasonable value of EA². However, the calculation of these corrections is a labourious numerical task.

A simple method for evaluation of EA of atoms is the use of an integral identity for the energy, derived in³. The basic idea in the derivation of this identity is the analytical continuation (into the complex k -plane) of the integral identity for the phase shifts δ_l ⁴

$$\operatorname{tg} \delta_l = -2 \int_0^{\infty} \hat{V}(r) f_l(k, r) j_l(kr) r dr. \quad (1)$$

The radial function $f_l(k, r)$ in (1) has the asymptotic behaviour

$$f_l(k, r) \underset{r \rightarrow \infty}{\sim} \sin \left(kr - \frac{l\pi}{2} \right) + \operatorname{tg} \delta_l \cos \left(kr - \frac{l\pi}{2} \right); \quad (2)$$

$j_l(kr)$ is the spherical Bessel function, and $V(r)$ is an one-particle potential operator. From the potential scattering theory it is well-known that the bound states of a particle in a potential $V(r)$ correspond to those pure imaginary values of the momentum $k_n = i\kappa_n$, for which (see e. g.⁴) p. 48)

$$\operatorname{tg} \delta_l(i\kappa_n) \rightarrow -i. \quad (3)$$

For s -bound states* of the electron in a negative atomic ion the relations (1) and (3) give an integral identity for κ ,

$$\kappa = -2 \int_0^{\infty} \hat{V}(r) \varphi(\kappa, r) \text{sh}(\kappa r) dr, \quad (4)$$

where $\varphi(\kappa, r)$ is the wave function of the loosely bound electron in the negative ion. It is obvious that the identity (4) can be used for evaluation of $EA = -\kappa^2/2$ by substituting for $\varphi(\kappa, r)$ an approximate function $\tilde{\varphi}(\kappa, r)$. Then the identity (4) gives an algebraic equation for κ . The validity of the result, of course, will depend on the choice of $\tilde{\varphi}(\kappa, r)$ and $V(r)$.

In this note we shall calculate the electron binding energy in Li ($1s^2 2s^2$). For $\tilde{\varphi}(\kappa, r)$ we shall take a hydrogenlike function

$$\tilde{\varphi}(\kappa, r) = Ar(1 - \kappa r)e^{-\kappa r}, \quad (5)$$

where A is the normalization constant.

In the potential $\hat{V}(r)$ we shall include the static interaction V_{st} of the electron with the atomic core, the exchange interaction with $2s$ and $2p$ states $\hat{W}(2s, 2p)$, and the polarization interaction V_p . Thus for $\hat{V}(r)$ we have

$$\hat{V}(r) = V_{st}(r) + \hat{W}_{2s, 2p}(r) + V_p(r), \quad (6)$$

where

$$V_{st}(r) = -\frac{z}{r} \sum_i \gamma_i e^{-\lambda_i r} \quad (7)$$

$$\begin{aligned} \hat{W} \tilde{\varphi} = & \pm 2 P_{2s}(r) \left\{ \frac{1}{r} \int_0^r P_{2s}(r') \tilde{\varphi}(\kappa, r') dr' + \int_r^{\infty} P_{2s}(r') \tilde{\varphi}(\kappa, r') \frac{dr'}{r} + \right. \\ & \left. + \left(E_{2s} + \frac{\kappa^2}{2} \right) \int_0^{\infty} P_{2s}(r') \tilde{\varphi}(\kappa, r') dr' \right\} \pm \frac{2 P_{2p}(r)}{3(E_{2s} - E_{2p})} \times \end{aligned}$$

* For l -bound state the integral identity for κ is

$$1 = 2i \int_0^{\infty} V(r) \varphi_l(\kappa, r) i_l(\kappa, r) r dr$$

where $i_l(x)$ is the modified spherical Bessel function.

$$\begin{aligned} & \times \frac{1}{r^2} \int_0^r P_{2s}(r') y_1(r'/P_{2s}, P_{2p}) \tilde{\varphi}(\kappa, r') r' dr' + \\ & + r \int_r^\infty P_{2s}(r') y_1(r'/P_{2s}, P_{2p}) \tilde{\varphi}(\kappa, r') \frac{dr'}{r'^2} \}, \end{aligned} \quad (8)$$

$$V_p(r) = \frac{[y_1(r/P_{2s}, P_{2p})]^2}{3(E_{2s} - E_{2p})}. \quad (9)$$

where

$$y_1(r/P_{2s}, P_{2p}) = \frac{1}{r^2} \int_0^r P_{2s}(r') P_{2p}(r') r' dr' + r \int_r^\infty P_{2s}(r') P_{2p}(r') \frac{dr'}{r'^2}, \quad (10)$$

and signs » + « and » — « correspond to the singlet and triplet states, respectively.

The «potential field parameters» γ_i and λ_i in (7) were taken from⁵⁾ and the functions $P_{2s}(r)$ and $P_{2p}(r)$ from⁶⁾ and (7), respectively.

The equation (4) has been solved numerically, and for the singlet state the result is $\kappa = 0,226$. The corresponding binding energy is $EA = 0,69$ eV.

For the triplet state no solution of equation (4) was found. The experimental value⁸⁾ for $EA_{(Li)}$ is 0,6 eV, while the variational method²⁾ gives a value of 0,58 eV. Edlén's⁹⁾ semiempirical value is 0,82 eV.

It was found that the exchange and the polarization terms in (6) very strongly affect the value of $EA_{(Li)}$, as in the case of $EA_{(H)}$ ³⁾.

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