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LETTER TO THE EDITOR

Many-body calculation of negative ions using the Dyson equation

L V Chernysheva†, G F Gribakin‡, V K Ivanov‡ and M Yu Kuchiev§

† Leningrad Institute of Informatics and Automatization of the Academy of Sciences of the USSR, Leningrad, USSR

‡ M I Kalinin Politechnical Institute, Leningrad, USSR

§ A F Ioffe Physical Technical Institute of the Academy of Sciences of the USSR, Leningrad, USSR

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Abstract. A new method of calculating atomic negative ions is developed. It is based on the Dyson equation, and gives the binding energy and the wavefunction of the outer electron in the negative ion. The calculation for He^- 1s2s2p ^4P is consistent with experiment. The photodetachment cross section for He^- ^4P is calculated for the first time. The phaseshift for p-electron quartet scattering by He 1s2s ^3S is presented. Results for the first calculation of Pd^- $4d^{10}5s$ ^2S are reported.

In this letter a new method of calculating atomic negative ions is suggested. The method is based on the Dyson equation within many-body theory (see e.g. Migdal 1983). Using this method we have calculated the characteristics of the He^- 1s2s2p ^4P negative ion, the photodetachment cross section for this ion and the phaseshift for p-electron quartet scattering by He 1s2s ^3S: (e^- + He 1s2s ^3S) ^4P. We have also carried out the first calculation of the $Pd^-4d^{10}5s$ ground state.

If an atom forms a stable negative ion with electron affinity EA > 0, its Green function $G_E(\boldsymbol{r}, \boldsymbol{r}')$ has a pole, when $E = \varepsilon_0 = -\text{EA}$:

$$G_E(\boldsymbol{r}, \boldsymbol{r}') \underset{E\to\varepsilon_0}{\approx} \frac{\varphi_0(\boldsymbol{r})\varphi_0^*(\boldsymbol{r}')}{E-\varepsilon_0}. \tag{1}$$

The quasiparticle wavefunction $\varphi_0(\boldsymbol{r})$ describes the motion of the outer electron in the negative ion. It is equal to the projection of the many-electron wavefunction $\Psi_0^{N+1}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N, \boldsymbol{r}_{N+1})$ of the negative-ion ground state to the atomic ground state wavefunction $\Psi_0^N(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$:

$$\varphi_0(\boldsymbol{r}) = \int \Psi_0^{N+1}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N, \boldsymbol{r}_{N+1})\Psi_0^{N*}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\, \mathrm{d}\boldsymbol{r}_1 \ldots \mathrm{d}\boldsymbol{r}_N. \tag{2}$$

The normalisation integral for $\varphi_0(\boldsymbol{r})$

$$a = \int |\varphi_0(\boldsymbol{r})|^2\, \mathrm{d}\boldsymbol{r} < 1 \tag{3}$$

gives the probability for the atomic core in the negative ion to be in the ground state. Usually a is close to unity, since the outer electron in the negative ion is localised mainly at large distances $r \sim R = \hbar(m_e \mathrm{EA})^{-1/2} \gg r_a$ (r_a is the neutral atom radius), perturbing the motion of atomic electrons weakly.

From this point of view the problem of the 'neutral atom + electron' system is to a certain extent a single-body problem. Indeed, it follows from the Dyson equation that the wavefunction $\varphi_0(\boldsymbol{r})$ and the energy ε_0 of the outer electron satisfy the equation

$$\varepsilon_0\varphi_0(\boldsymbol{r}) = \hat{H}^{(0)}\varphi_0(\boldsymbol{r}) + \int \Sigma_{\varepsilon_0}(\boldsymbol{r}, \boldsymbol{r}')\varphi_0(\boldsymbol{r}')\, \mathrm{d}\boldsymbol{r}'. \tag{4}$$

Here $\hat{H}^{(0)}$ is the electron Hamiltonian in the static atomic field, and the non-local, energy-dependent potential $\Sigma_E(\boldsymbol{r}, \boldsymbol{r}')$ is the self-energy of the single-particle Green function. The latter describes the dynamical interaction of the outer electron with atomic electrons. At large distances $\Sigma_E(\boldsymbol{r}, \boldsymbol{r}')$ in (4) turns into the well known polarisation potential $-\alpha_d e^2/2r^4$, α_d being the dipole static polarisability of the atom.

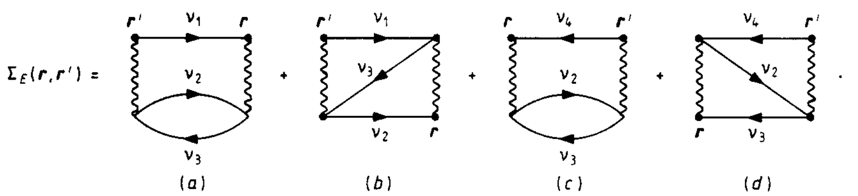
Formerly the equation (4) was used to calculate correlational corrections to the electron–atom scattering phaseshifts (Kelly 1967, Amusia *et al* 1975, 1985), and to the wavefunction and energy of the outer electron in alkali-metal atoms (Lindgren *et al* 1976, Dzuba *et al* 1985). The peculiarity of the negative-ion problem is that the correlational potential $\Sigma_E(\boldsymbol{r}, \boldsymbol{r}')$ plays a decisive role when binding the electron to the atom; hence it cannot be taken into account by perturbations.

Let $\hat{H}^{(0)}$ be a Hartree–Fock Hamiltonian of the neutral atom. The spectrum of the Hartree–Fock equation

$$\hat{H}^{(0)}\varphi_\nu^{(0)}(\boldsymbol{r}) = \varepsilon_\nu\varphi_\nu^{(0)}(\boldsymbol{r}) \tag{5}$$

consists of discrete states, occupied in the atomic ground state ($\varepsilon_\nu < 0$), and excited states of electron in the field of the neutral atom. For most atoms the latter belong to the continuum ($\varepsilon_\nu > 0$), so that negative ions do not exist within the static, Hartree–Fock approximation.

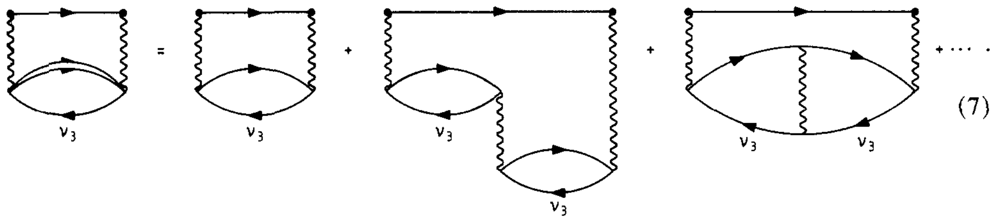
The ratio r_a/R is small. Thus, in the range of typical outer electron distances $r, r' \sim R$ $\Sigma_E(\boldsymbol{r}, \boldsymbol{r}')$ can be calculated as a series in orders of the interaction of the outer electron with atomic electrons. Using the notation of standard atomic diagrams (see e.g. Amusia and Cherepkov 1975), we obtain in the lowest second order:



(6)

At large distances $r, r' \sim R$ the diagrams (6c, d) are exponentially small, since the vertices $\boldsymbol{r}, \boldsymbol{r}'$ contain occupied state (hole) wavefunctions. The main contribution to $\Sigma_E(\boldsymbol{r}, \boldsymbol{r}')$ arises from diagram (6a) with the dipole $\nu_3 \to \nu_2$ excitation, its magnitude being proportional to R^{-4}. The exchange diagram (6b) should be included for Pauli's principle to be valid.

The essential part of intra-atomic correlations can be taken into account by calculating the wavefunction of the ν_2 excited state in the field of the atomic core with a hole ν_3 (Amusia *et al* 1975). Denoting this wavefunction with a double line, we obtain for (6*a*):



(7)

Equation (4) has the most simple form in the matrix representation in terms of the complete orthonormalised set of Hartree–Fock wavefunctions $\varphi_\nu^{(0)}(\boldsymbol{r})$:

$$\varepsilon_0 C_\nu = \varepsilon_\nu C_\nu + \sum_{\nu'} \langle \nu | \Sigma_{\varepsilon_0} | \nu' \rangle C_{\nu'} \tag{8}$$

where

$$C_\nu = \int \varphi_\nu^{(0)*}(\boldsymbol{r}) \varphi_0(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}$$

and correspondingly

$$\varphi_0(\boldsymbol{r}) = \sum_\nu C_\nu \varphi_\nu^{(0)}(\boldsymbol{r}). \tag{9}$$

The summation in (8) and (9) takes into account both discrete and continuous spectra. To find ε_0 and C_ν it is necessary to solve the eigenstate problem for the matrix (integral operator):

$$\varepsilon_\nu \delta_{\nu\nu'} + \langle \nu | \Sigma_E | \nu' \rangle \qquad (E = \varepsilon_0). \tag{10}$$

The self-energy $\Sigma_E(\boldsymbol{r}, \boldsymbol{r}')$ varies slowly with E, when $|E| \ll I$, I being the atomic ionisation potential. Since $|\varepsilon_0| \ll I$, one can ignore the dependence of matrix (10) on energy, and compute it with $E \approx 0$. Accordingly, the normalisation integral (Migdal 1983)

$$a = \left(1 - \frac{\partial \varepsilon_0(E)}{\partial E}\bigg|_{E=\varepsilon_0}\right)^{-1} \tag{11}$$

is close to unity, due to $|\partial\varepsilon_0(E)/\partial E| \sim |\varepsilon_0|/I \ll 1$.

The above theory can be readily applied to atoms with non-degenerate ground state, binding an extra electron into the unoccupied subshell. In order to test the method we have calculated the simple negative ion of He^- 1s2s2p ^{4}P. This long-lived ($\tau \sim 10^{-5}$ s) ion is formed by the binding of a p electron to the excited metastable atomic state He 1s2s ^{3}S. Formerly the binding energy was calculated using the configuration interaction method (Bunge and Bunge 1984) that yields EA(He ^{3}S) = 77.51 meV $\simeq$ 0.0057 Ryd. This value is in good agreement with the experimental one (Peterson *et al* 1985): 77.5 ± 0.8 meV.

The Hartree–Fock spectrum of the p electron for He 1s2s ^{3}S does not contain discrete states. When the electron momentum k vanishes, the p phaseshift tends to zero (see figure 1). In our calculations the continuous energy spectrum was approximated by the appropriate finite set of states, equidistant in momentum with Δk step

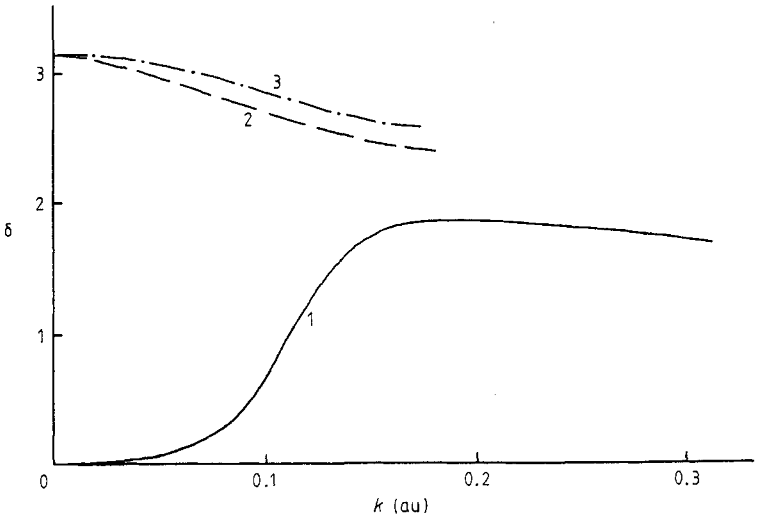
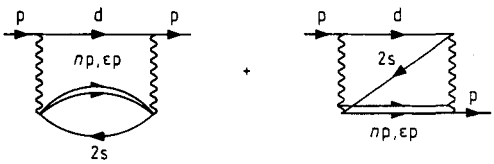
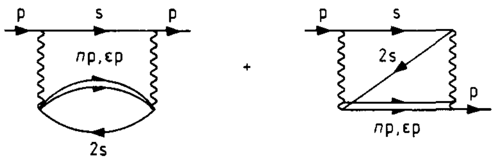


Figure 1. The p phaseshift for electron quartet scattering by He 1s2s ^{3}S: curve 1, Hartree–Fock approximation; 2, with main self-energy diagram (12*a*) taken into account; 3, with three diagrams (12*a*–*c*) taken into account.

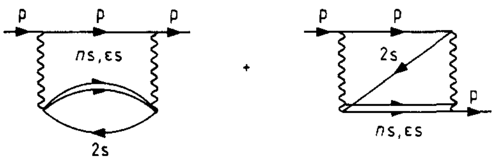
size. The conditions $k_{\min} \ll \sqrt{|\varepsilon_0|} \ll k_{\max}$, $\Delta k \ll \sqrt{|\varepsilon_0|}$ were observed to make the decomposition (9) correct. The computer code of Chernysheva *et al* (1980) was used to calculate the self-energy matrix, and to obtain phaseshifts with correlations taken into account. The self-energy matrix included the following second-order diagrams with dipole, monopole and quadrupole excitations of He 1s2s ^{3}S:



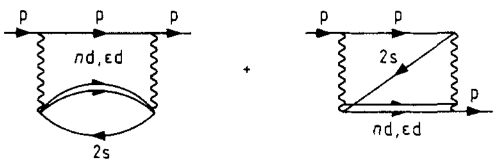
−0.813 (12*a*)



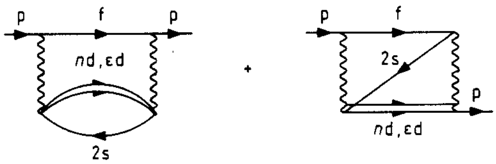
−0.182 (12*b*)



−0.358 (12*c*)



0.220 (12*d*)



$$-0.062. \qquad (12e)$$

To compare the relative importance of various self-energy diagrams, the maximal in modulus values of the amplitudes are presented. The sum of dipole diagrams (12*a*, *b*) indeed gives the leading contribution to the correlational potential. In (12*a*, *b*) 2s→2p atomic excitation dominates over the others, and the rate of exchange diagrams is roughly 30% of the direct ones.

With only the main diagram (12*a*) included in $\langle \nu | \Sigma_E | \nu' \rangle$, the p-phaseshift behaviour substantially changed (figure 1, curve 2). According to Levinson's theorem, it means that a discrete level arose in the system. Diagonalising (10) we obtained $\varepsilon_0 = -0.0004$ Ryd. The corresponding radial wavefunction, obtained from (9), is shown in figure 2. Addition of the second dipole (12*b*) and monopole (12*c*) diagrams to the self-energy matrix varied the phaseshift weakly (figure 1), but noticeably increased the binding energy: $\varepsilon_0 = -0.0095$ Ryd (figure 2, curve 2).

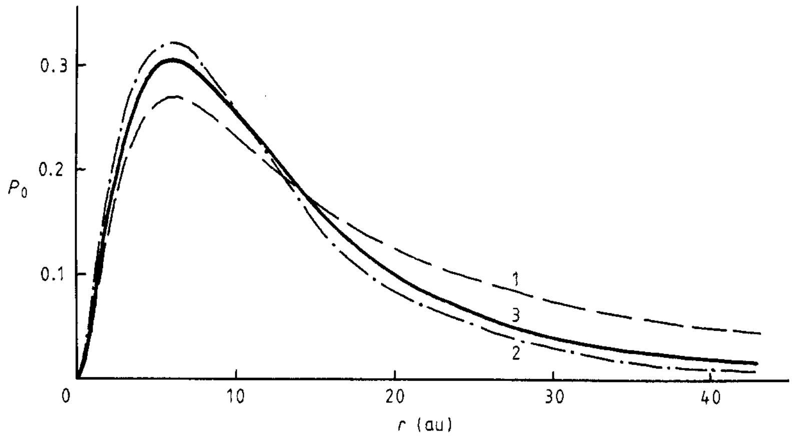


Figure 2. Radial 2p-electron wavefunction in He^- 1s2s2p ^4P: 1, with main self-energy diagram (12*a*) taken into account ($\varepsilon_0 = -0.0004$ Ryd); 2, with three diagrams (12*a*–*c*) taken into account ($\varepsilon_0 = -0.0095$ Ryd); 3, with five diagrams (12*a*–*e*) taken into account ($\varepsilon_0 = -0.0062$ Ryd).

The magnitude of diagrams (12*d*, *e*) with quadrupole excitation of the atom is essentially less than that of the dipole ones. The largest among (12*d*, *e*) is the exchange diagram in (12*d*), because it consists of quadrupole and dipole matrix elements, while the direct diagram consists of two quadrupole matrix elements. Thus, the sum of (12*d*, *e*) is positive. Taking into account all diagrams (12) we obtain: $\varepsilon_0 = -0.0062$ Ryd. This result is quite close to the exact binding energy for the 2p electron in He^- 1s2s2p ^4P. To obtain a more precise value one should calculate second-order diagrams with higher multipole atomic excitations, together with diagrams of higher orders. However, their total contribution to the self-energy is limited to 3–5%.

The wavefunction for the 2p electron in He^- ^4P, corresponding to $\varepsilon_0 = -0.0062$ Ryd, is shown in figure 2 by the full curve. Using a Hartree–Fock wavefunction in the field of He 1s2s ^{3}S for the photoelectron in the final state, the dipole amplitude for 2p photodetachment was calculated. Cross sections in 2p→εd and 2p→εs channels, obtained with **r**- and **∇**-forms of the dipole operator, are presented in figure 3 as functions of photon energy $\hbar\omega$. The 2p→εd channel dominates in the dipole sum rule, yielding 1.41 and 0.77 for **r**- and **∇**-forms respectively. The difference between the two forms is due to the fact that we neglect the action of $\Sigma_E(\boldsymbol{r}, \boldsymbol{r}')$ onto the final-state photoelectron, together with correlational corrections to the electron–photon vertex. The calculation of these corrections forms the subject of a special detailed study.

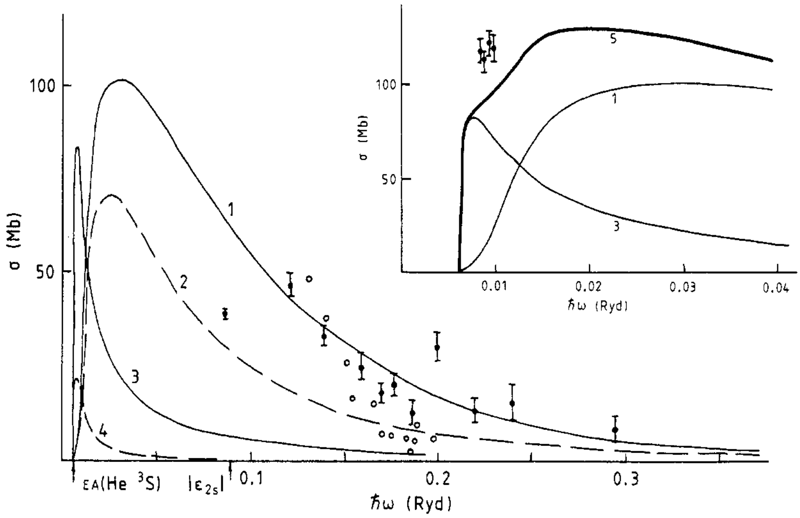


Figure 3. Photodetachment cross sections for He$^-$ 1s2s2p ^{4}P. Calculation: 1, 2p→εd channel, **r**-form; 2, **∇**-form; 3, 2p→εs channel, **r**-form; 4, **∇**-form; 5, total 2p-photodetachment cross section, **r**-form. Experiment: ○, Compton *et al* (1980); ⧳, Hodges *et al* (1981).

Photodetachment cross sections for He$^-$ ^{4}P, measured by Compton *et al* (1980) and Hodges *et al* (1981), are shown in figure 3. The accuracy of the experiments is estimated by their authors to be 20–30%. The 2s-photodetachment threshold is situated at $\hbar\omega = |\varepsilon_{2s}| = 0.090$ Ryd. The cross section in this channel is concentrated in a very narrow energy range above the threshold (Peterson *et al* 1985). Thus, the calculated 2p-photodetachment cross section is consistent with the experimental total cross sections.

Besides the rather simple He$^-$ ^{4}P ion we have considered the ion Pd$^-$ 4d^{10}5s ^{2}S, formed by the binding of an s electron to a Pd 4d^{10} ^{1}S atom. Its electron affinity EA(Pd) = 0.557 eV = 0.041 Ryd and configuration were established in the experiment of Feigerle *et al* (1981). In the preliminary calculation second-order diagrams with monopole, dipole (these are of chief importance) and quadrupole excitations of the 4d subshell were included in the self-energy matrix, giving $\varepsilon_0 = -0.0104$ Ryd for the 5s-electron energy. This result unambiguously confirms the existence of the Pd$^-$ ion with the 4d^{10}5s configuration. To obtain a more accurate binding energy value, thorough investigation and estimation of various self-energy diagrams are necessary.

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