A NEW METHOD OF CALCULATING THE SPECTRUM AND THE SELF-CONSISTENT FIELD OF NEGATIVE IONS

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A new method is suggested for negative ion calculations, based on perturbation theory with a model zeroth approximation and a polarization potential formalism. The binding energy of an electron in an Na⁻ ion is calculated as a test, and is found to agree with experiment.

1. As is well-known, the binding energy (BE) of an electron in negative ions is one of the most important characteristics of these systems, and is required in the construction of kinetic models in plasma processes, in developing gas lasers and radiation sources, and in a large number of other applications [1-4]. The available experimental methods do not allow total coverage of the large group of ions needed for these applications. The contemporary a priori methods of atomic calculations are valid in calculating transition energies, ionization potentials, and term splitting, but the calculation of BE in negative ions (NI) is a very complicated problem. The use of simplified models [5, 6] to solve this problem does not always provide results satisfying accurately the requirements of applications. Most NIs cannot generally be correctly described within the single-particle approximation, such as the Hartree—Fock (HF) approximation, since their total HF-energy is higher than the HF-energy of the ground state of the atom [7]. This implies that a correct NI calculation necessarily requires account of many-particle correlations. Most successful is, obviously, the method of many-body theory, particularly the approach using the solution of the Dyson equations with properly determined eigenenergy functions of Σ, for which, however, one requires accurate, quite awkward treatment of the contributions of various processes to Σ (see [8, 9]). A new effective approach is suggested in the present study of calculating the spectrum of bound states and, in particular, determination of electron BE in an NI, based on the polarization potential method and perturbation theory with a model zeroth approximation [10-12]. Based on these methods, it has been possible to enhance the spectroscopic accuracy in describing a wide range of properties of atomic systems (see [13-21]). Though relativisitic effects do not play a substantial role in most NIs, except heavy ions, following the purpose of including the NI calculation method in the most general complex of atomic programs, the treatment below is carried out within the relativistic approximation.

2. For definiteness consider the Na⁻ NI (configuration $3s^2$ ^1S), for which there exists a quite accurate measurement of the BE experimental value: EA = 0.5479 eV. To find the true value it is required to calculate the ground state energy of Na⁻, as well as the energy value of neutral Na, which is well known. For correct Na⁻ calculation one requires accurate account of interelectron correlations, including in our approach effects of order higher than second order perturbation theory (PT) of the Rayleigh—Schrodinger type. The complete Na⁻ Hamiltonian can be written in the following form (with account of the comments on behavior of relativistic effects)

$$H = \sum_i h(r_i) + \sum_{ij} e^{i\omega r_{ij}} \left[\frac{1}{r_{ij}} - \frac{(\alpha_i r_{ij})(\alpha_j r_{ij})}{r_{ij}^3} \right],$$ (1)

where α_i, α_j are Dirac matrices. The single-particle wave function of the zeroth approximation is determined by the Dirac equation, in which the eigenvalue is the empirical electron energy E_{3s}, and the potential is

$$H_0 = \sum_i h(r_i) + \sum_i V_c(r_i | b).$$ (2)

where

$$V_c(r \mid b) = 2\left[1 - e^{-2r}(1 + r)\right]/r +$$
$$+ 8\left[1 - e^{-br}\left(1 + \frac{3}{4}br + \frac{1}{4}b^2r^2 + \frac{1}{16}b^3r^3\right)\right]\bigg/r. \tag{3}$$

The model potential V_c describes the interaction of the external 3s electron with the core of filled electron shells $1s^2 2s^2 2p^6$. The choice of analytic shape of the potential V_c was motivated in [17], and b is an adjustable parameter. A correctly selected value guarantees satisfaction of the conditions

$$f(r) \to 0, \quad g(r) \to 0, \quad r \to \infty, \tag{4}$$

where f(r), g(r) are the large and small components of the wave functions determined by the solution of the Dirac equation. The perturbation operator is

$$H_{\text{int}} = \sum_{ij} e^{i\omega r_{ij}}\left[\frac{1}{r_{ij}} + (\boldsymbol{\alpha}_i\, r_{ij})\,(\boldsymbol{\alpha}_j\, r_{ij})/r_{ij}^3\right] - \sum_i V_c(r_i \mid b), \tag{5}$$

where $e_{ij}{}^{i\omega r}$ is a delay factor, and the summation is carried out over the total number of electrons. In relativistic theory, structured on the Dirac wave functions, the Breit operator includes only retardation and magnetic interaction effects [18]. One further calculates the energy matrix within the j—j coupling scheme of angular momenta; transition to the intermediate coupling scheme is realized by diagonalization of the secular matrix. The energy of state $E(3s^2\ {}^1S)$ is represented in the form of a PT series

$$E(n_2 l_2 j_2 n_1 l_1 j_1) = E_{e\ell}^{(0)}(n_2 l_2 j_2) + E_{e\ell}^{(Q)}(n_1 l_1 j_1) + \Delta E^{(1)} + \Delta E^{(2)}, \tag{6}$$

where $E_{e\ell}^{(0)}$ is the single-particle electron energy over the core $1s^2 2s^2 2p^6$ (being referred to the total core energy). For the electron $E^{(0)}$ is determined by the first ionization potential of the Na atom and by the electron transition energies over the Na core [16, 17]. The single-particle energies provide a contribution to the diagonal elements only. The experimental information included in the zeroth approximation already contains the major portion of all correlation and relativistic effects. Within first order PT one calculates the matrix element of the interparticle interaction operator on wave functions of external electrons:

$$\Delta E^{(1)} = <n_1 l_1 j_1 n_2 l_2 j_2\,[JM_J]\,\frac{e^{i\omega r_{12}}}{r_{12}}\,n_1' l_1' j_1' n_2' l_2' j_2'\,[JM_J]> =$$
$$= [(2j_1' + 1)(2j_2' + 1)(2j_1 + 1)(2j_2 + 1)]^{1/2} \times$$
$$\times \left[\sum_a (-1)^{1 + j_1 + j_2' + a + J}\begin{Bmatrix} a & j_1 & j_1' \\ J & j_2' & j_2 \end{Bmatrix}\begin{pmatrix} j_1 & j_1 & a \\ 1/2 & -1/2 & 0 \end{pmatrix}\begin{pmatrix} j_2' & j_2 & a \\ 1/2 & -1/2 & 0 \end{pmatrix}\times \right.$$
$$\times \{al_1 l_1'\}\{al_2 l_2'\}\,R_a(n_1 l_1 j_1 n_2 l_2 j_2;\ n_2' l_2' j_2' n_1' l_1' j_1') + (2J + 1)^{-1} \times$$
$$\left. \times (-1)^{j_2' + j_1 + 1}\begin{pmatrix} j_1 & j_2 & J \\ 1/2 & -1/2 & 0 \end{pmatrix}\begin{pmatrix} j_2' & j_1 & J \\ 1/2 & -1/2 & 0 \end{pmatrix}\{Jl_1 l_2\}\{Jl_1' l_2'\}\,R_J(n_1 l_1 j_1 n_2 l_2 j_2;\ n_1' l_1' j_1',\ n_2' l_2' j_2')\right]. \tag{7}$$

Account of retardation effects has led to replacement of the usual combination $U_a(r_1 r_2) = \dfrac{r_<^a}{r_>^{a+1}}$ in the radial integrals by the expression $\tilde{U}_a(r_1 r_2) = U_a(r_1 r_2) Z_1(r_1) Z_2(r_2)$, where Z_1, Z_2 are modified Bessel functions. In each order of PT, starting from the first, there exist vacuum diagrams (without free edge), single-particle diagrams (one pair of free edges), two-particle (for two pairs of free edges), etc. (Fig. 1). The vacuum diagrams (A) describe only the reference point, therefore their contribution vanishes. The contributions of single-particle diagrams (B) of all orders are directly determined by experimental information concerning the vanishing approximation. The first order two-particle diagrams (C) provides in the case of an electron the contribution (7) to the total energy. Within first order there exist no two-particle diagrams with a compensating term to H_{int}: $-V_c$. Within second order, however, such diagrams appear, but their contribution is compensated by diagrams with self-energy insertions (or HF). Consider the second order two-particle diagrams D1, D2, D3 (Fig. 1b), for which the calculation must be carried out. Correlations are usually included by imposing additional configurations, i.e., extending the secular matrix. The additional configurations can be partitioned into two groups: 1) states with electron excitation from the core; states
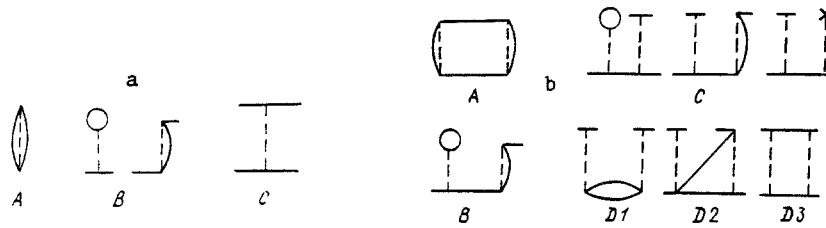
Fig. 1. Feynman diagrams for perturbation theory energy
corrections: a) first, b) second order.

with a single vacancy and three electrons outside the core; their imposition includes the polarization interaction of exterior electrons with each other (the diagrams D1, D2); 2) states corresponding to excitation of one of the exterior particles (the number of exterior particles does not change in this case); their application describes the external screening effect of the exterior particles with each other (the diagram D3). These two state types provide the second order PT correction $\Delta E^{(2)} = \Delta E_{pol}^{(2)} + \Delta E_{scr}^{(2)}$. Characteristically, this additive partitioning is possible only within second order; in higher orders diagrams occur describing interference of these effects. The inclusion of states of the first type has led to calculations of otherwise awkward matrix elements; states of the second type can be included, in principle, in the secular matrix by expression (7) directly. Here, however, it seems that it is necessary to include the whole continuum of higher order states to achieve the required accuracy. An effective method of taking into account states of both types without increasing the size of the secular matrix was suggested in [16], and consists of supplementing the Coulomb interparticle interaction operator by a polarization operator, describing the interaction of exterior particles in terms of a polarizable core. According to [16], the matrix elements of the polarization operator are contributions of the direct and exchange polarization diagrams

$$\Delta E_{pol}^{(2)} = \iint dr_1 dr_2 \rho_1(r_1) [V_{pol}^{d}(r_1 r_2) + V_{pol}^{ex}(r_1 r_2)] \rho_2(r_2),$$

where ρ_1, ρ_2 are the density distributions for exterior electrons, and

$$V_{pol}^{d}(r_1, r_2) = X\{\int dr \rho_c^{(0)1/3}(r)/|r_1 - r||r - r_2| -$$
$$- [\int dr \rho^{(0)1/3}(r)/|r_1 - r| \int dr' \rho_c^{(0)1/3}(r')/|r' - r_2|/I]\};$$

$$V_{pol}^{ex}(r_1 r_2) = - \frac{X}{2}(0,375)^{1/3} [(\rho_c^{(0)1/3}(r_1) + \rho_c^{(0)1/3}(r_2))/|r_1 - r_2| -$$
$$- \int dr \rho_c^{(0)2/3}(r) \{\rho_c^{(0)-1/3}(r_1)/|r_1 - r| + \rho_c^{(0)-1/3}(r_2)/|r - r_2|\}/I],$$

$$I = \int dr \rho_c^{(0)1/3}(r).$$

Here X is a numerical coefficient, with the procedure of finding it given in [16], and $\rho_c^{(0)}$ is the electron density of the core in the absence of exterior electrons. The angular parts of the matrix elements V_{pol}^{d}, V_{pol}^{ex}, r_{12}^{-1} coincide, therefore account of the corrections $\Delta E_{pol}^{(2)}$ reduces to modification of the radial integrals appearing in the expression for $\Delta E^{(1)}$, whose analytic form is given in [16]. The introduction of V_{pol} made it possible to reduce the problem to a two-particle problem accurately within second order PT. Account of the screening effect of the exterior electrons can be carried out, adding to the interaction potential of the exterior electron with the core in the vanishing approximation in the Hamiltonian an additional screening potential, generated by the presence of the second particle: $W(r) = \int dr' \Psi_{n\ell j}^2(r')/r_>$, where $r_>$ is the larger of r and r'. Calculation has shown (see [16]) that for any state of the screening particle the potential W is well-approximated by the expression

$$W(r|g) = g/Z(3+gr)/(3+2gr+2g^2 r^2),$$

where $g = Z/n^2(Z + N)$, N is the number of electrons in the core, Z is the nuclear charge, and n is the principal quantum number. The potentials $W(r)$ and $W(r|g)$ coincide asymptotically for $r \to \infty$, while for $g = \int \frac{dr'}{r'} \Psi_{n\ell j}^2$ they also coincide for $r \to 0$. The parameter g can be found from the minimization condition of the ground state. Inclusion of $W(r|g)$ in the zeroth order makes it possible to account effectively for ladder type diagrams of all PT or-

ders (Fig. 1). The procedure consists of the following phases: 1) for each exterior particle state $n\ell j$ one solves the Dirac equation with Hamiltonian H_0, in which one uses experimental data on ionization energies $E_{n\ell j}$ to determine the parameters of the potential $V_c(r \mid b)$; 2) in the single-electron equation, for each exterior particle one introduces the potential $W(r \mid g)$, and the new orbital energies are found. The final form of the zeroth approximation potential is

$$V_c(r_1 \mid b) + V_c(r_2 \mid b) + W(r_1 \mid g) + W_2(r_2 \mid g) - Z/r_1 - Z/r_2,$$

and the perturbation is

$$e^{i\omega r_{12}}/r_{12} + V_{pol}(r_1 r_2) - [V_c(r_1 \mid b) + V_c(r_2 \mid b) + W(r_1 \mid g) + W(r_2 \mid g)];$$

3) with the new orbitals one calculates the radial integrals and the energy matrix; from the diagonal elements of the energy matrix $<n_1 l_1 j_1 n_2 l_2 j_2 [J] \dfrac{e^{i\omega r_{12}}}{r_{12}} n_1 l_1 j_1 n_2 l_2 j_2 [J]>$ one calculates the quantity

$$<n_1 l_1 j_1 \mid W(r \mid g) \mid n_1 l_1 j_1> + <n_2 l_2 j_2 \mid W(r \mid g) \mid n_2 l_2 j_2>,$$

i.e., the matrix element of the second compensating term in the perturbation operator. The calculation procedure practically accounts for the whole second order correction $\Delta E^{(2)}$, as well as some part of higher order PT corrections.

3. The BE calculation of an electron in the Na⁻ ion, carried out on the basis of the method described, provided the following value: EA = 0.546 eV, in very good agreement with the experimental value. We stress that even though for definiteness we selected the Na⁻ NI, the method suggested can be used in treating and calculating arbitrary, more complex NIs with one or several electrons outside the core of filled electron shells. In this case one requires an accurate choice of the corresponding treated system of the model potential (for example, the universally modified Thomas-Fermi potential, used in the well-known program of atomic calculations "SUPER-STRUCTURE," etc.), and the total energy calculation requires assembly of the energy matrix and its subsequent diagonalization. In the case of an NI with a single electron outside a core of filled shells the whole problem reduces to solving a Dirac equation with a model plus a polarization potential.

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