A method of solving the quasiparticle equation for atoms

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Relative coordinates spanning connected manifolds are employed to describe the internal motion of multielectron atoms. By using differential operations on connected manifolds, the quasiparticle equation for atoms is found and an approximate method for its solution is proposed. The method is tested by calculations of the ground and excited states of the helium atom and of the ground state of some two-electron ions.

The many-electron motion in atoms and molecules is usually described by absolute (independent) coordinates. Among these are the position sectors with the origin fixed at a point. The many-electron Schrödinger equation in the absolute frame is integrated numerically, and in the course of solution one somehow has to take into account the cooperative features of the many-electron motion (mutual screening of electron distributions, variation of the effective potentials, and so on). For example, the kinetic part of the two-electron Schrödinger equation in the absolute frame

$$\left[\frac{\hbar^2}{2m}(\Delta_1+\Delta_2)+e^2\left(\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{1}{r_{12}}\right)+E\right]\psi=0, \tag{1}$$

(where m is the electron mass, Z is the nuclear charge, and $r_{12} = |\mathbf{r}_{12} - \mathbf{r}_2|$) does not reflect the effective variation of the masses, and the screening effect of the electron distributions is only allowed for in the repulsive potential.

To avoid numerical integration and take better account of the cooperative features of many-electron motion, use can be made of relative coordinates[1]. The relative vectors connect particles in pairs and thus have no common origin. Both the beginnings and the ends of these vectors vary connectedly in a many-particle motion. For example, the relative coordinates of a three-particle system are connected by the following identity

$$\boldsymbol{\eta}_1+\boldsymbol{\eta}_2+\boldsymbol{\eta}_3\equiv0, \tag{2}$$

and the virtual displacements of their ends are connected by the limiting relations[2]

$$(\delta\boldsymbol{\eta}_i/\delta\boldsymbol{\eta}_j)\,|_{\eta_k}=-1 \qquad (i\neq j\neq k). \tag{3}$$

Neglecting the center-of-mass motion, we obtain for the helium atom and two-electron ions the following equation[1] in the relative coordinates:

$$\left[\sum_{j=1}^{3}\frac{\hbar^2}{2\mu_j}\Delta_j+e^2\left(\frac{Z}{\eta_1}+\frac{Z}{\eta_3}-\frac{1}{\eta_2}\right)+E\right]\psi(\boldsymbol{\eta}_1,\boldsymbol{\eta}_2,\boldsymbol{\eta}_3)\approx0, \tag{4}$$

where the effective masses are

$$\mu_1=\mu_3\approx m, \qquad \mu\approx m/A \tag{5}$$

(since the nuclear mass is A times greater than the electron mass). Δ_j is the Laplacian formally defined in the space of the relative vector η_j. The latter equation is supplemented with the conditions[1]:

$$[\nabla_1+A\nabla_2+\nabla_3]\psi=0, \qquad \boldsymbol{\eta}_1+\boldsymbol{\eta}_2+\boldsymbol{\eta}_3\equiv0, \tag{6}$$

where ∇_j are formally defined gradients with respect to the relative vectors η_j.

A system of a finite number of particles n corresponds to a figure composed of the triangles[2]

$$\gamma_i\boldsymbol{\eta}_i+\gamma_j\boldsymbol{\eta}_j+\gamma_k\boldsymbol{\eta}_k\equiv0 \qquad (i\neq j\neq k=1,\ldots,N), \tag{7}$$

where γ_i, γ_j, and $\gamma_k = \pm1$, and $N = n(n-1)/2$. Consequently, the relative coordinates can be also used to describe the many-electron motion in the presence of a finite number of attractive centers, i.e., in molecules.

It should be added that quantum equations stipulated in the relative coordinates are not equivalent to corresponding Schrödinger's equations. Nevertheless, the quantum equations for atoms and molecules can be solved by approximate analytical methods and the results obtained are in good agreement with experiment. This can be comprehended if we note that the relative coordinates represent another means of describing the many-particle motion, and that the existing analysis is not adequate to infer the structure of the connected manifolds they span. It is, moreover, possible to construct differential operations on connected manifolds, which lead to symmetric equations for the many-particle motion.

1. QUASIPARTICLE EQUATION FOR ATOMS

In order to have a natural definition of the differential operations on the connected manifolds (2), we choose the relative coordinates to be equivalent[2], and employ the limit relations (3). The solution of Eq. (4) is then sought in its natural form of a product

$$\psi(\boldsymbol{\eta}_1,\boldsymbol{\eta}_2,\boldsymbol{\eta}_3)=\prod_{j=1}^{3}\psi_j(\boldsymbol{\eta}_j). \tag{8}$$

With this product we evaluate the relative gradients

$$\begin{gathered}\nabla_1\psi=(\nabla_1\psi_1)\psi_2\psi_3-\psi_1(\nabla_2\psi_2)\psi_3-\psi_1\psi_2(\nabla_3\psi_3),\ldots\\ \nabla_3\psi=-(\nabla_1\psi_1)\psi_2\psi_3-\psi_1(\nabla_2\psi_2)\psi_3+\psi_1\psi_2(\nabla_3\psi_3).\end{gathered} \tag{9}$$

Next, the formal operator condition (6) is replaced by an approximate (to within 2/A) relation

$$(\nabla_1\psi_1)\psi_2\psi_3-\psi_1(\nabla_2\psi_2)\psi_3+\psi_1\psi_2(\nabla_3\psi_3)\approx0. \tag{10}$$

In order to transform Eq. (4) to equivalent coordinates, we evaluate three relative Laplacians:

$$\begin{gathered}\Delta_i\psi=(\Delta_1\psi_1)\psi_2\psi_3+\psi_1(\Delta_2\psi_2)\psi_3+\psi_1\psi_2(\Delta_3\psi_3)\\ -2[(\nabla_i\psi_i)(\nabla_j\psi_j)\psi_k+(\nabla_i\psi_i)\psi_j(\nabla_k\psi_k)-\psi_i(\nabla_j\psi_j)(\nabla_k\psi_k)],\end{gathered} \tag{11}$$

where $i \neq j \neq k$. Next, we find the scalar products of the relative gradients by successively applying the operators to the approximate equation (8). These products are excluded from the relative Laplacians.

$$\Delta_1\psi\approx4\psi_1\psi_2(\Delta_3\psi_3), \qquad \Delta_2\psi\approx0, \qquad \Delta_3\psi\approx4(\Delta_1\psi_1)\psi_2\psi_3, \tag{12}$$

This enables us to consider the function $\psi_2(\eta_2)$ approximately constant, inasmuch as it is not acted upon by differential operators. We then obtain the following quasiparticle equation for the helium atom and helium-like ions:

$$\frac{2\hbar^2}{m}[(\Delta_1\psi_1)\psi_3+\psi_1(\Delta_3\psi_3)]+\left[e^2\left(\frac{Z}{\eta_1}+\frac{Z}{\eta_3}-\frac{1}{\eta_2}\right)+E\right]\psi_1\psi_3\approx 0, \qquad (13)$$

This equation is essentially different from the two-electron Schrödinger equation (1) in that its effective mass is four times less than the electron mass and the relative coordinates vary connectedly. The quasiparticle equation is solved without the additional condition (9), as the latter has been employed in the transformations.

In a similar way one obtains a quasiparticle equation for many-electron atoms by choosing in the triads (7) the relative coordinates to be equivalent.

2. METHOD OF SOLUTION OF THE QUASIPARTICLE EQUATION

In solving the quasiparticle equation (13) we employ proportional coordinates

$$\xi_i=\eta_i/2. \qquad (14)$$

In terms of the latter the kinetic part of the equation consists of "hydrogen-like" operators

$$\frac{\hbar^2}{2m}[(\Delta_1\psi_1)\psi_3+\psi_1(\Delta_3\psi_3)]+\left[\frac{e^2}{2}\left(\frac{Z}{\xi_1}+\frac{Z}{\xi_3}-\frac{1}{\xi_2}\right)+E\right]\psi_1\psi_3\approx 0, \qquad (15)$$

and the unit of energy becomes four times less than the corresponding atomic unit.

As has been shown previously[2], the binding energy of a close system of particles of identical mass is given by a sum of $n(n-1)/2$ integrals of relative motion. But inasmuch as the masses of electrons are very small compared to those of nuclei, the binding energy of a two-electron atom, while remaining constant, can in the mean be represented by a sum of the functions

$$E=\frac{e^2}{2s}\left[-\frac{\sigma_1}{\xi_1}-\frac{\sigma_3}{\xi_3}+\frac{1}{\xi_2}\left(1-\sum_{\gamma=1}^{\infty}s^{\gamma+1}\frac{\xi_2^{\gamma}}{\langle\xi_2^{\gamma}\rangle}\right)\right], \qquad (16)$$

where σ_1 and σ_3 are unknown screening parameters, s is an unknown parameter of convergence-in-the-mean of the iteration series, and $\langle\ldots\rangle$ denotes averaging in the zeroth approximation. The Coulomb repulsion energy is expressed from (16) as follows

$$\frac{e^2}{2\xi_2}=sE+\frac{e^2}{2}\left[\frac{\sigma_1}{\xi_1}+\frac{\sigma_3}{\xi_3}+\sum_{\gamma=1}^{\infty}s^{\gamma+1}\frac{\xi_2^{\gamma-1}}{\langle\xi_2^{\gamma}\rangle}\right]. \qquad (17)$$

Next we obtain a transformed quasiparticle equation which explicitly takes into account the mutual screening of electron distributions

$$(\Delta_{\xi_1}\psi_1)\psi_3+\psi_1(\Delta_{\xi_3}\psi_3)+\left[\frac{Z_1}{\xi_1}+\frac{Z_3}{\xi_3}+2(1-s)E\right]\psi_1\psi_3 \approx\sum_{\gamma=1}^{\infty}s^{\gamma+1}\frac{\xi_2^{\gamma-1}}{\langle\xi_2^{\gamma}\rangle}\psi_1\psi_3, \qquad (18)$$

where we assume $\hbar = m = e = 1$, and denote $Z_1 = Z - \sigma_1$ and $Z_3 = Z - \sigma_3$.

If $|s| < 1$, as is the case in applications, then the series of averaged perturbation terms in Eq. (18) converges absolutely and the magnitude of its mean sum turns out to be smaller than the average Coulomb repulsion energy. If one neglects the perturbation series, then the proportional coordinates in the unperturbed part of Eq. (18) become uncoupled. Therefore, in the zeroth approximation the binding energy of a two-electron atom equals the sum of the binding energies of two quasiparticles:

$$E_0=\varepsilon_{n_1l_1}+\varepsilon_{n_3l_3}, \qquad (19)$$

where n_k and l_k are the principal and the orbital quasiparticle quantum numbers. Then, in the same approximation for the unperturbed part of the quasiparticle equation we have an equivalent system of two equations

$$\left[\Delta_{\xi_k}+\frac{Z_{n_kl_k}}{\xi_k}+2(1-s)\varepsilon_{n_kl_k}\right]\psi_{0n_kl_k}(\xi_k)\approx 0, \qquad (20)$$

which are to be solved under the limit conditions

$$\lim_{\xi_k\to\infty}\psi_{0n_kl_k}(\xi_k)=0. \qquad (21)$$

The solutions of the equivalent equations with the conditions (21) are known[3]. Along with the eigenvalues

$$\varepsilon_{n_kl_k}=-(Z-\sigma_{n_kl_k})^2/8(1-s)n_k^2 \qquad (22)$$

they prove to be functions of the unknown parameters.

To find these parameters, we observe that each electron in the atom corresponds to one quasiparticle, and therefore we must assign to each of the latter the value of spin of the corresponding electron. Next, from the quasiparticle functions multiplied by the electron spin functions we form in the zeroth approximation an antisymmetric atomic wave function which will again depend on the unknown parameters.

The parameters are evaluated in the zeroth approximation by omitting the iteration series in (16). Upon averaging we obtain the following algebraic equation

$$\frac{s}{4(1-s)}\left[\frac{Z^2_{n_1l_1}}{n_1^2}+\frac{Z^2_{n_3l_3}}{n_3^2}\right]=\left\langle\frac{\sigma_{n_1l_1}}{\xi_1}+\frac{\sigma_{n_3l_3}}{\xi_3}-\frac{1}{\xi_2}\right\rangle. \qquad (23)$$

Next we recognize that the difference between the average attractive potential without screening (in the absence of the Coulomb repulsion) and the mean attractive potential for the screened motion must be equal for each electron to its portion of the average repulsive Coulomb energy. We then obtain two more algebraic equations:

$$\left\langle\frac{Z}{\eta_k}\right\rangle'-4\left\langle\frac{Z-\sigma_{n_kl_k}}{\eta_k}\right\rangle=4\frac{n_k+l_k}{(n_1+l_1)+(n_3+l_3)}\left\langle\frac{1}{\eta_2}\right\rangle', \qquad (24)$$

where the dash specifies the average over the unscreened motion, and the factors of four at the averages over the screened motion are to ensure the use of the atomic units of energy.

To obtain higher approximations, Eq. (18) is successively multiplied by each of the conjugate quasiparticle wave functions and the average is taken over the approximate motion:

$$\left[\Delta_k+\frac{Z_{n_kl_k}}{\xi_k}+2(1-s)\varepsilon_{n_kl_k}-2W_k(\xi_k)\right]\psi_{n_kl_k}(\xi_k)\approx 0, \qquad (25)$$

where W_k is the average value of the perturbing term. The perturbed equations of the obtained equivalent system are then solved by usual methods of the perturbation theory[4].

The quasiparticle equation for many-electron atoms is solved in the proportional coordinates in a similar way.

3. SIMPLEST ATOMS AND IONS

We shall illustrate the method by calculating the helium atom and some helium-like ions in the ground state. In this state $n_1 = n_3 = 1$ and $l_1 = l_3 = 0$. The wave functions in the zeroth approximation for both the screened and the unscreened motion are proportional to the corresponding products

$$\psi_{010}(\xi_1,\xi_3)\sim\exp[-Z_1(\xi_1+\xi_3)/2] \quad (Z_1=Z-\sigma),$$
$$\varphi_{10}(\eta_1,\eta_3)\sim\exp[-Z(\eta_1+\eta_3)]. \qquad (26)$$

The zeroth approximation for the binding energy in the atomic units is given by

$$E_0 = -(Z-\sigma)^2/(1-s). \tag{27}$$

Next, from (23) and (24) we obtain two algebraic equations to evaluate the unknown nonvarying parameters:

$$\frac{s}{1-s} = \frac{16\sigma-5}{8(Z-\sigma)}, \quad \sigma = \left(Z+\frac{5}{32}\right) - Z\left[1+\frac{25}{1024Z^2}\right]^{1/2}. \tag{28}$$

In our calculations we first evaluate those parameters that are not subject to variation. Then we determine the atomic binding energies and ionization potentials in the first approximation for eigenvalues.

In the table, Z is the nuclear charge, s is the convergence parameter, σ is the screening constant, E are the calculated binding energies, J_t are the calculated ionization potentials and J_e are their experimental values[5]. One readily finds from the table that, as the nuclear charge increases, the parameter s approaches zero, while the screening constant virtually does not change. Consequently, at large Z expression (27) tends to its physically obvious limit Z^2.

In conclusion it should be noted that our method employs Hartree's idea of an effective potential. Its interpretation, however, is different, since the effective potentials are incorporated directly in the equations of the motion. In our calculations we also use the Fock approximation in which the atomic wave functions are chosen to be antisymmetric. It is difficult to compare our method with that of Hartree-Fock by iterations because the computational schemes are essentially different.

	s	σ	E, eV	J_t, eV	J_e, eV
He	−0.213	0.150	78.889	24.412	24.58
Li+	−0.127	0.152	198.077	75.498	75.62
Be²+	−0.090	0.153	371.755	153.817	153.85
B³+	−0.070	0.154	599.921	259.384	259.40

Nevertheless, there is a way of comparison. The amount of computational work by the Hartree-Fock method is known to be much larger for calculations of excited atomic states than for those of ground states. By the indicated method for the $(1s)^1(2s)^2$ configuration of orthohelium in the first approximation for eigenvalues we calculated (without computers) the convergence parameter s = −0.0486, the effective electronic charges $Z_1 = 2.0031$ and $Z_2 = 1.8663$, and the ionization potential 0.36 Ry, which is in agreement with the experimental value 0.35 Ry[3]. The results obtained show that the charge distribution of the first unexcited electron is slightly contracted by that of the excited electron.

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