Asymptotic behavior of atomic wave functions

G. K. Ivanov and M. A. Kozhushner

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 117977 Moscow, Russia
(Submitted 30 April 1993)

We use the Lippmann–Schwinger equation to study the asymptotic behavior of the wave function of a multielectron atom in which one electron is in the remote subbarrier region and the rest are in the fundamental region of motion. The proposed integral-equation approach automatically ensures the correct radial and angular asymptotic dependence, and makes it possible to derive the asymptotic coefficients, expanded in terms of the ionic states and the spherical harmonics of the individual electron, all to the same accuracy as provided by a quantum-chemical calculation of the atomic and ionic wave functions.

1. INTRODUCTION

An understanding of wave function behavior in multiparticle systems (atoms, molecules, clusters, etc.) is required for the solution of a broad range of problems associated with electron tunneling and the interaction of widely separated atomic particles. Such problems include charge exchange, spin exchange, electron and heavy-particle tunneling in condensed media and chemical reactions, electron tunneling in scanning electron microscopes, Josephson junctions, and so on.

Actual calculations of asymptotic wave functions for atoms and simple molecules (mathematical studies can be found in Refs. 1–6) have until recently been based upon matching the electron wave function at the boundary between two rather different regions of electron motion[3,7]: the asymptotic (remote subbarrier) region, and the region of fundamental motion (see the relevant discussion in Ref. 7). We use the one-electron approximation in the asymptotic region, where the effective potential depends on the Coulomb interaction with the ionic core. In the region of fundamental motion, the problem is manifestly a multielectron one, and we make use of conventional quantum-chemical numerical methods (Hartree–Fock and other variational approaches). The two solutions are obliged to match up at electron coordinate values where neither type of solution is entirely valid. Here the matching can only be carried out effectively in the one-dimensional case, so in finding the asymptotic behavior of atomic wave functions, those functions corresponding to a fixed orbital angular momentum are the ones to be matched.

This idea presupposes that the asymptotic wave function of an orbital electron takes the form[1]

$$\Psi_{nlm}(r,\theta,\varphi) = C_{nl} Y_{lm}(\theta,\varphi) r^{1/\alpha-1} e^{-\alpha r}, \qquad (1)$$

where $\alpha = (2I)^{1/2}$ is related to the electron's ionization potential I, and n, l, and m are the quantum numbers of the individual electron orbital being matched. An atomic wave function can then be constructed out of valence-electron orbitals (1) in the genealogical approximation of Ref. 3. In view of the aforementioned peculiarities of the matching

method, we believe that nothing further can be said about the accuracy of the asymptotic coefficients C_{nl} that it produces.

Ivanov and Kozhushner[8,9] proposed a way to find the asymptotic behavior of one-electron wave functions for molecules and molecular centers using the Lippmann–Schwinger equation, and their approach was extended to arbitrary multielectron systems in Ref. 10. In the present paper, we use this integral equation method to formulate a general algorithm for constructing asymptotic wave functions of atoms and ions. Actual calculations have been carried out for He, Be, C, and Sc (the latter being the simplest atom with an outer s shell and an unfilled d shell).

2. INTEGRAL EQUATION METHOD

We apply the integral equation method here to multielectron systems. We write the Hamiltonian of an N-electron atom in the form

$$H = -\frac{1}{2} \sum_{k=2}^{N} \Delta_k - \frac{1}{2} \Delta_1 + u(\{r_{N-1}\}) - \frac{1}{r_1}$$
$$+ V(r_1,\{r_{N-1}\}) = H_0 + V(r_1,\{r_{N-1}\}). \qquad (2)$$

Here r_1 is the position of an individual electron whose asymptotic behavior we wish to investigate in the remote subbarrier region, $\{r_{N-1}\}$ is the set of coordinates of the other $N-1$ electrons, Δ_k is the Laplacian with respect to the coordinates of the kth electron, $u(\{r_{N-1}\})$ is the potential energy of the $N-1$ electrons,

$$V(r_1,\{r_{N-1}\}) = \sum_{k=2}^{N} \frac{1}{|r_1-r_k|} - \frac{Z-1}{r_1}$$
$$= \sum_{k=2}^{N} \left[\frac{1}{|r_1-r_k|} - \frac{1}{r_1} \right]$$
$$= \sum_{k=2}^{N} \sum_{n=0}^{\infty} Q_n(r_1,r_k) \qquad (3)$$

is the residual interaction potential between the selected (first) electron and the ion after subtraction of the long-range Coulomb potential, Z is the charge on the atomic nucleus, the terms Q_n in (3) are given by

$$Q_n(r_1,r_k) = \frac{4\pi}{2n+1}\, \eta_n(r_1,r_k) \sum_{\lambda=-n}^{n} Y_{n\lambda}^*\!\left(\frac{\mathbf{r}_1}{r_1}\right) Y_{n\lambda}\!\left(\frac{\mathbf{r}_k}{r_k}\right), \qquad (4)$$

where $Y_{n\lambda}(\mathbf{r}_i/r_i)$ is a spherical harmonic expressed in terms of the angular coordinates of the ith electron, and

$$\eta_0 = (r_1,r_k) = \begin{cases} -\dfrac{1}{r_1} + \dfrac{1}{r_k}, & r_1 \leqslant r_k \\[2mm] 0, & r_1 > r_k \end{cases} \qquad (4a)$$

$$\eta_n(r_1,r_k) = \begin{cases} \dfrac{r_1^n}{r_k^{n+1}}, & r_1 \leqslant r_k \\[3mm] \dfrac{r_k^n}{r_1^{n+1}}, & r_1 > r_k \end{cases} \quad (n \geqslant 1). \qquad (4b)$$

For a system with the Hamiltonian (2), the Lippmann–Schwinger equation takes the form

$$\Psi(\mathbf{r}_1,\{\mathbf{r}_{N-1}\};E)$$

$$= \int d\mathbf{r}_1' d\{\mathbf{r}_{N-1}'\} G(\mathbf{r}_1,\{\mathbf{r}_{N-1}\},\mathbf{r}_1'\{\mathbf{r}_{N-1}'\};E)$$

$$\times V(\mathbf{r}_1',\{\mathbf{r}_{N-1}'\})\Psi(\{\mathbf{r}_N'\},E). \qquad (5)$$

Here G is the Green's function for the Hamiltonian H_0 in a system with total energy E. The different notation for the wave function Ψ of the entire system on the left- and right-hand sides of (5) stems from the fact that we wish to derive the asymptotic behavior of Ψ as a function of $\mathbf{r}_1$. For simplicity we omit spin variables, which are normally summed over.

Since the interaction between the first electron and all the remaining ones does not appear in the Hamiltonian H_0, the spectral representation of the Green's function immediately yields

$$G(\mathbf{r}_1,\{\mathbf{r}_{N-1}\},\mathbf{r}'\{\mathbf{r}_{N-1}'\},E)$$

$$= \sum_p \phi_p^*(\{\mathbf{r}_{N-1}\}) G_1(\mathbf{r}_1,\mathbf{r}_1';E-\varepsilon_p)\phi_p(\{\mathbf{r}_{N-1}'\}), \qquad (6)$$

where ϕ_p and ε_p are the energy eigenfunctions and eigenvalues of the $N-1$-electron ion, p is the corresponding set of quantum numbers, ε_p is reckoned from the ionic ground state, so that $E = -I$ (i.e., E is the ionization potential of the atom), and G_1 is the one-electron Green's function, which corresponds to motion of the first electron in a Coulomb potential.

On the right-hand side of (5), Ψ and ϕ_p are assumed to have been symmetrized as necessary, since they are eigenfunctions of the atomic and ionic Hamiltonians, which are symmetric under electron exchange. On the other hand, because the first electron has been singled out, the Hamiltonian H_0 is not symmetric under exchange of the first and other electrons, and $\Psi(\mathbf{r}_1 \to \infty,\{\mathbf{r}_{N-1}\})$ has not been symmetrized under the exchange $\mathbf{r}_1 \leftrightarrow \mathbf{r}_k (k \geqslant 2)$, although it is an eigenfunction of H. The appropriate procedure should be carried out as well.

The basic idea underlying our approach is that Eq. (5) can be considered essentially an expression with which one can determine the asymptotic value (as $r_1 \to \infty$) of the

function on the left-hand side of (5) in terms of an integral over atomic and ionic wave functions, which are determined within the fundamental region of motion using quantum-chemical methods of some sort. This requires that the integration on the right-hand side of (5) be carried out over exactly that region, which for the $(N-1)$ electrons remaining in the ion occurs automatically by virtue of the exponential falloff of the atomic and ionic wave functions. We can show that this requirement is also satisfied when one integrates over the coordinates of the first electron.

Starting with G_1 expressed in spherical harmonics,

$$G_1(\mathbf{r}_1,\mathbf{r}_1';\varepsilon) = \sum_{lm} g_l(r_1,r_1';\varepsilon) Y_{lm}^*\!\left(\frac{\mathbf{r}_1}{r_1}\right) Y_{lm}\!\left(\frac{\mathbf{r}_1'}{r_1'}\right), \qquad (7)$$

we can use the well-known expression for the radial Coulomb Green's function with $r \gg r'$ and $r \gg 1/|\varepsilon|$, yielding

$$g_l(r_1,r;\varepsilon) = R_{\kappa l}(r')T(r), \qquad (8)$$

$$T(r) = -\frac{1}{r}(2\kappa r)^{1/\kappa} e^{-\kappa r}, \qquad (9)$$

$$R_{\kappa l}(r') = \frac{\Gamma\!\left(l+1-\dfrac{1}{\kappa}\right)}{(2l+1)!}(2\kappa r')^l e^{-\kappa r'}$$

$$\times F\!\left(-\frac{1}{\kappa}+l+1,\, 2l+2,\, 2\kappa r'\right), \qquad (10)$$

where $\kappa = (-2\varepsilon)^{1/2}$, and $F(\alpha,\gamma,Z)$ is the degenerate hypergeometric function.

Substituting (6)–(9) into (5), we obtain

$$\Psi(r_1 \to \infty,\{\mathbf{r}_{N-1}\};E) = \sum_p B_p \phi_p(\{\mathbf{r}_{N-1}\}) r_1^{1/\kappa_p-1} e^{-\kappa_p r_1}, \qquad (11)$$

$$B_p = 2(2\kappa_p)^{1/\kappa_p} \sum_{lm} Y_{lm}^*\!\left(\frac{\mathbf{r}_1}{r_1}\right) \int d\mathbf{r}_1' d\{\mathbf{r}_{N-1}'\} Y_{lm}\!\left(\frac{\mathbf{r}_1'}{r_1'}\right)$$

$$\times R_{\kappa_1 l}(r')\phi_p(\{\mathbf{r}_{N-1}'\}) \sum_{k=2}^{N}\sum_{n=0}^{\infty} Q_n(r_1',r_k')\Psi(\{\mathbf{r}_N'\};E)$$

$$\kappa_p = [-2(E-\varepsilon_p)]^{1/2}. \qquad (12)$$

Consistent with the fact that the electron moves in a pure Coulomb potential far from the core, it follows from (11) that the asymptotic atomic wave function is a superposition of asymptotic Coulomb wave functions (1) for various ionic states.

For $r' \gg 1/\kappa_p$, F in (10) goes asymptotically as

$$F\!\left(-\frac{1}{\kappa}+l+1,\, 2l+2,\, 2\kappa r'\right) \sim (r')^{-l-1-1/\kappa} e^{2\kappa r'},$$

and thus, according to (10),

$$R_{\kappa l}(r') \sim (r')^{-1-1/\kappa} e^{\kappa r'}.$$

We see that in accordance with (1) and (11), the integrand in (12) goes as $(r_1')^{-2}V(\mathbf{r}_1',\{\mathbf{r}_{N-1}'\})$. After integrating over the coordinates of all electrons except the first,

the potential V falls off at least as fast as $(r_1')^{-2}$, since there is no Coulomb interaction $V(\mathbf{r}_1',\{\mathbf{r}_{N-1}'\})$ between the first electron and the ion. The potential does include interactions like charge-dipole, charge-quadrupole, etc. [see Eqs. (4a) and (4b)]. The integral over r_1' in (12) therefore converges as a power of r_1' (at least as fast as $dr_1'/r_1'^2$). We can thus assume that the integral in (12) is dominated by the inner region of the atom, where the quantum-chemically calculated wave functions of the atoms and ions are accurately known. The asymptotic coefficients obtained from (12) should therefore be at least as accurate.

Note that atomic wave functions calculated variationally normally fall off faster than $e^{-\kappa r_1'}$, which means that the integral over r_1' converges not just as a power of r_1', but exponentially.

3. CALCULATION OF ANGULAR DEPENDENCES AND ASYMPTOTIC COEFFICIENTS

The LS coupling scheme holds for atoms in the first half of the periodic table, where S is the total spin quantum number, and L is the total orbital angular momentum. In this approximation, the total atomic or ionic wave function in a state with given total angular momentum j and projection M_j can be written

$$|jM_jSL\rangle = \sum_{M_L M_S} \begin{bmatrix} S & L & j \\ M_S & M_L & M_j \end{bmatrix} |\gamma SM_SLM_L\rangle, \quad (13)$$

where the $\begin{bmatrix} S & L & j \\ M_S & M_L & M_j \end{bmatrix}$ are Clebsch–Gordan coefficients, and γ represents the nonangular quantum numbers of the system.

We can calculate the asymptotic coefficients B_p for the functions $|\gamma SM_SLM_L\rangle$; their magnitudes depend mainly on the quantum numbers of the atom (SL) and ion (S_pL_p), since it is these that determine the appropriate sets of Slater determinants—and thus the wave functions—that enter into the integral in (12). Moreover, B_p depends on the spin projections of the atom and ion. This dependence can be established in general form. As in the genealogical coefficient scheme, the atomic wave function can be written in the form

$$|\gamma SM_SLM_L\rangle = \sum_{\substack{L_pM_p \\ S_pM_{S_p}}} B_p^0 \begin{bmatrix} \frac{1}{2} & S_p & S \\ \sigma & M_{S_p} & M_S \end{bmatrix} \begin{bmatrix} l & L_p & L \\ m_l & M_p & M_L \end{bmatrix}$$

$$\times r_1^{1/\kappa_p-1}e^{-\kappa_p r_1}\phi_p\chi_{1/2\sigma}. \quad (14)$$

Here $\chi_{1/2\sigma}$ is the spin function of the first electron, and the coefficient of the product $r_1^{1/\kappa_p-1}e^{-\kappa_p r_1}\phi_p$ is in fact the asymptotic coefficient B_p. The dependence of B_p on M_L, M_p, M_S, and M_{S_p} (B_p^0 is independent of all of these) is given explicitly by the two Clebsch–Gordan coefficients spelled out in Eq. (14). The calculation can therefore be carried out for a particular set of determinants corresponding to fixed quantum numbers M_L, M_p, M_S, and M_{S_p}, and (14) can then be used to proceed to the general case.

The functions $\Psi(\{\mathbf{r}_N\},E)$ and $\phi(\{\mathbf{r}_{N-1}\})$ in Eq. (12) can be represented by a superposition of Slater determinants constructed out of various sets of atomic (or ionic) spin orbitals:

$$\varphi_{\mu,\nu}^{a,i}(r,\sigma) = f_{nl}^{a,i}(r)Y_{lm}\left(\frac{\mathbf{r}}{r}\right)\chi_{1/2\sigma},$$

$$\Psi(\{\mathbf{r}_N\};E) = \sum_g A_g^a \mathrm{Det}_g\{\varphi_\mu^a(\mathbf{r}_k,\sigma_k)\},$$

$$\phi_p(\{\mathbf{r}_{N-1}\}) = \sum_t A_p^i \mathrm{Det}_t\{\varphi_\nu^i(\mathbf{r}_k,\sigma_k)\},$$

where superscripts a and i denote atomic and ionic orbitals, μ and ν denote the set of quantum numbers nlm, $\mathrm{Det}_{g,t}\{\varphi_{\mu,\nu}^{a,i}(\mathbf{r}_k,\sigma_k)$ is the determinant constructed from the g,t set of μ, ν orbitals of the atom or ion, and the coefficients A_g^a and A_p^i can be determined in the usual way, starting with specific values of μ, ν and L,S.

Having substituted (14) into (12), we find that a typical term in the sum in (12) is proportional to

$$\mathscr{L}_{\tilde{n}_1,\tilde{l}_1,\tilde{m}_1;\tilde{n}_k\tilde{l}_k\tilde{m}_k}^{n_1l_1m_1;n_kl_km_k} = \left\langle \varphi_{n_kl_km_k}^i(\mathbf{r}_\kappa,\sigma_\kappa)R_{\kappa_pl_1}(r_1)Y_{l_1m_1}\left(\frac{\mathbf{r}_1}{r_1}\right)\chi_{1/2\sigma_1}\right|$$

$$\times \sum_{n=0}^\infty Q_n(\mathbf{r}_1,\mathbf{r}_k)|\varphi_{\tilde{n}_k\tilde{l}_k\tilde{m}_\kappa}^a(\mathbf{r}_k,\sigma_k)\varphi_{\tilde{n}_1\tilde{l}_1\tilde{m}_1}^a(\mathbf{r}_1,\sigma_1)\rangle$$

$$\times \prod_{s\neq 1,k}\langle \varphi_{n_sl_sm_s}^i(\mathbf{r}_s,\sigma_s)|\varphi_{\tilde{n}_s\tilde{l}_s\tilde{m}_s}^a(\mathbf{r}_s,\sigma_s)\rangle, \quad (15)$$

which can be interpreted as the probability amplitude of detecting the first electron in a subbarrier state with quantum numbers $n_1l_1m_1$, having made a transition from the atomic $\tilde{n}_1\tilde{l}_1\tilde{m}_1$ state by virtue of its interaction with the κth electron, whose orbital quantum numbers are $\tilde{n}_k\tilde{l}_k\tilde{m}_k$ (in the atom) and $n_kl_km_k$ (in the ion). We see, then, that all nonvanishing superpositions of angular integrals contribute to the asymptotic wave function with given angular momentum l_1.

Note that in general, the radial parts of the atomic and ionic orbitals in (15) are not orthogonal to one another, although there have been calculations indicating that this lack of orthogonality can be neglected without seriously affecting accuracy.

Since the interaction $V=\Sigma_{k=2}^N\Sigma_{n=0}^\infty Q_n$ in (15) is invariant under rotation of the coordinate system, the system's total orbital angular momentum L is conserved (as is the total spin S). Given atomic and ionic quantum numbers L and L_p, we then have

$$|L-L_p|\leqslant l_1\leqslant L+L_p. \quad (16)$$

The desired asymptotic wave function is then given by a superposition of spherical harmonics $Y_{l_1m_1}(\mathbf{r}_1/r_1)$ with coefficients given by (15).

Excited ionic states often have a low excitation energy $\varepsilon_p\ll I$ (especially among the transition elements). The actual asymptotic behavior at $r_1\lesssim\sqrt{I/\varepsilon_p}$, according to (11), will then be determined by a complete set of ionic states—both the ground state and excited states—which can result in a large variety of angular dependences $B(\theta_1,\varphi_1)$, and

can alter the magnitude of the coefficient B itself, which is used to determine the electron density far from the core. This should be taken into account in problems requiring that one find the electron density at large radii—for example, in elastic (for an atom) peripheral electron scattering.

If we consider electronic transitions (e.g., charge exchange) in which the ion's final state p_f is fixed, the transition probability will then be governed solely by the asymptotic function corresponding to that fixed state, with an asymptotic coefficient B_{p_f}.

As usual, we can choose the radial parts of the atomic and ionic orbitals to be of the form

$$f_{nl}(r) = \sum_v q_v \, r^v e^{-\alpha_v r}, \tag{17}$$

so all of the integrals in (15) can be calculated analytically and represented in terms of hypergeometric functions $_1F_1$.

It has been assumed in (12) that we sum over the $(N-1)$ electrons that interact with the selected electron (which penetrates the subbarrier region), and this automatically allows for all possible orbital states nl that enter into the atomic and ionic wave functions [see (15)]. Obviously, however, not all orbitals contribute equally to the coefficient B_p in question.

The matrix element (15) takes the form of a transition amplitude induced by the interaction (4) from a state with an atomic wave function to a state more aptly described as an ion plus an electron. Orbitals in inner and outer atomic shells make significantly different contributions, by virtue of where they are localized.

Three basic combinations are possible when there is more than one electron in the outer shell:

1) the quantum numbers $\mu_1 = (n_1 l_1 m_1)$ of the ejected electron and κth electron interacting with it (μ_k and ν_k) refer to the outer shell of the atom and ion;

2) μ_1 is from the outer shell, μ_k and ν_k from an inner shell;

3) μ_1 is from an inner shell, μ_k and ν_k from the outer.

The first of these combinations is normally the main contributor, due to conditions being more conducive to overlap of the wave functions. In the second case, the integration region is determined by the way in which the inner-electron wave function dies out, and in the third, the matrix element corresponds to a transition of the κth electron from the outer shell to an inner shell. In general, then, the second and third combinations should contribute less than the first. Calculations show that in practice, it is usually sufficient to include only the contribution of the outer shell and the filled (or unfilled) shell nearest in energy. This greatly simplifies calculations for multielectron atoms.

4. CALCULATIONS FOR SPECIFIC ATOMS

Helium

We have used a variety of wave function approximations, each providing different accuracy in the calculated atomic ionization potential.

For the first calculation, we used

$$\Psi_{1s}^a = \frac{\alpha^3}{8\pi^3} e^{-1/2\alpha(r_1+r_2)}, \quad \alpha = 3,4,$$

which yields the ionization potential to 7% accuracy. We obtained $B=2.52$ for the ion's ground state.

A calculation using the more accurate Hylleraas three-parameter wave function[11] for the He atom, which allows for interelectron correlation and yields the potential to 0.1% accuracy, gives $B=2.45$.

Clearly, the accuracy of the coefficient B roughly corresponds to the integrated accuracy of the wave function, which is dictated by the energy of the system. Note that the value of B obtained by matching wave functions is $B=2.87$.[7]

Beryllium

In the beryllium atom, two electrons occupy the inner $1s$ shell, and two occupy the outer $2s$ shell. The orbitals contributing to the Slater determinant are

$$\varphi_{1s}^{a,i} = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha r},$$

$$\varphi_{2s}^{a,i} = \sqrt{\frac{3\beta^5}{\pi(\alpha^2-\alpha\beta+\beta^2)}} \left(1-\frac{\alpha+\beta}{3}r\right)e^{-\beta r}, \tag{18}$$

and the corresponding atomic and ionic parameters are

$$\alpha=3.708, \quad \beta=1.159$$

$$\alpha=3.697 \quad \beta=1.328.$$

Substituting into (12) the atomic and ionic wave functions obtained in the one-determinant approximation with the orbitals (18), we obtain (here, according to (16), the asymptotic wave function contains only an s wave)

$$B_0 \sim \int d\mathbf{r}_1' d\mathbf{r}_2' R_{\kappa 0}(r_1') \left(\frac{1}{|\mathbf{r}_1-\mathbf{r}_2'|}-\frac{1}{r_1'}\right)$$

$$\times \{\varphi_{2s}^a(\mathbf{r}_1')\varphi_{2s}^a(\mathbf{r}_2')\varphi_{2s}^i(\mathbf{r}_2')$$

$$+2\varphi_{2s}^a(\mathbf{r}_1')\varphi_{2s}^a(\mathbf{r}_2')\varphi_{1s}'(\mathbf{r}_2')$$

$$-\varphi_{1s}^a(\mathbf{r}_1')\varphi_{2s}^a(\mathbf{r}_2')\varphi_{1s}'(\mathbf{r}_2')\}. \tag{19}$$

In (19), the terms in curly brackets from the various shells have been assigned according to the foregoing classification scheme. By chance (because of interference), the contribution of the first term turns out to be anomalously small. The resulting contributions to $B=B_1+B_2+B_3$ are $B_1=-0.015$, $B_2=-0.720$, and $B_3=-0.157$, yielding $B=-0.890$. Allowance only for the contribution of the outer electrons to the asymptotic behavior of Be yields a manifestly incorrect result (two orders of magnitude too small). Note that our value of B differs appreciably from $B=1.62$, the value obtained by matching wave functions.[7]

Carbon

In considering carbon, we took account of the four outer $2s^2 2p^2$ electrons. The atomic ground state is ^3P, and the ionic is ^2P. The atomic and ionic wave functions can be

expressed as a sum of Slater determinants constructed out of the orbitals in the simplest two-exponential approximation.[13]

For the sake of definiteness, we assume that M, the projection of the orbital angular momentum, is either $M_a = 1$ (atom) or $M_i = 0$ (ion), so the orbitals contributing to Ψ_a are φ_{11}^a and φ_{10}^a, while ϕ_p contributes to ϕ_{10}^i. Substituting Ψ and ϕ_p into (12), we find that the asymptotic wave function comprises four terms $P_i, i = 1,2,3,4$, where each P_i is associated with the asymptotic behavior in a specific way [see the explanation following Eq. (15)]:

1) P_1 corresponds to $\mu_1 = n_1 l_1 m_1 = (2,1,1), \mu_k = (2,0,0), \nu_k = (2,0,0)$,

2) P_2 corresponds to $\mu_1 = (2,0,0), \mu_k = (2,1,1), \nu_k = (2,0,0)$,

3) P_3 corresponds to $\mu_1 = (2,1,0), \mu_k = (2,1,1), \nu_k = (2,0,0)$,

4) P_4 corresponds to $\mu_1 = (2,1,1), \mu_k = (2,1,0), \nu_k = (2,1,0)$.

At first glance, according to (16), s, p, and d asymptotic terms should be possible, in principle. But due to the structure of the integrals over angle, the s and d waves vanish identically, and only the P wave remains in the asymptotic wave function. The atomic state with $M = 1$ and the ionic state with $M = 0$ then correspond to the asymptotic atomic wave function

$$\Psi(\mathbf{r}_1 \to \infty, \{\mathbf{r}_{N-1}\}) = B^0 Y_{11}\left(\frac{\mathbf{r}_1}{r_1}\right) r_1^{1/\kappa - 1} e^{-\kappa r},$$

with $B^0 = 1.26$ in contrast to $B^0 = 0.92$, the value obtained by matching wave functions.[7]

Scandium

The scandium atom is the first of the transition metals with an unfilled d shell. The ground state is ^2D: one electron is in the $3d$ shell, and there are two electrons in the outer unfilled $4s$ shell. In our calculations, we took the Sc atom to be a three-electron system, and the ion was a two-electron system with two ionic states—the ^3D ground state, and a low-lying ^1D excited state (excitation energy $\varepsilon_1 = 4900$ cm^{-1}).

Due to the differing spins of the ground and excited states of the ion, the ionic wave functions can be described by various combinations of Slater orbitals. As a result, we obtain the asymptotic coefficients

$$B_0 \sim \int d\mathbf{r}_1' d\mathbf{r}_2' V(\mathbf{r}_1', \mathbf{r}_2') \, [\varphi_s^a(\mathbf{r}_1') \varphi_s^a(\mathbf{r}_2') \varphi_s^i(\mathbf{r}_2') R_{\kappa l}(\mathbf{r}_1')$$

$$+ \varphi_s^a(\mathbf{r}_1') \varphi_d^a(\mathbf{r}_2') \varphi_d^i(\mathbf{r}_2') R_{\kappa l}(\mathbf{r}_1')] , Y_{lm}\left(\frac{\mathbf{r}_1'}{r_1}\right), \quad (20)$$

$$B_1 \sim \int d\mathbf{r}_1' d\mathbf{r}_2' V(\mathbf{r}_1', \mathbf{r}_2') \, [-\varphi_s^a(\mathbf{r}_1') \varphi_s^a(\mathbf{r}_2') \varphi_s^i(\mathbf{r}_2') R_{\kappa l}(\mathbf{r}_1')$$

$$+ \varphi_d^a(\mathbf{r}_1') \varphi_s^a(\mathbf{r}_2') \varphi_d^i(\mathbf{r}_2') R_{\kappa l}(\mathbf{r}_1')$$

$$- \varphi_s^a(\mathbf{r}_1') \varphi_d^a(\mathbf{r}_2') \varphi_d^i(\mathbf{r}_2') R_{\kappa l}(\mathbf{r}_1')] , Y_{lm}\left(\frac{\mathbf{r}_1'}{r_1}\right), \quad (21)$$

where we have used the simple analytic approximations to the $4s$ and $3d$ atomic and ionic orbitals suggested in Ref. 12 for $\varphi_s^a, \varphi_s^i, \varphi_d^a, \varphi_d^i$.

We have found that the only combinations that are important for B_0 are

$$\mu_1 = (4,0,0), \quad \mu_k = (4,0,0), \quad \nu_k = (4,0,0),$$

$$\mu_1 = (4,0,0), \quad \mu_k = (3,2,m_a), \quad \nu_k = (3,2,m_i).$$

Other combinations are spin-forbidden. The contribution to B_1, on the other hand, comes from a large number of combinations

$$\mu_1 = (4,0,0), \quad \mu_k = (4,0,0), \quad \nu_k = (4,0,0),$$

$$\mu_1 = (3,2,m_1), \quad \mu_k = (4,0,0), \quad \nu_k = (3,2,m_i),$$

$$\mu_1 = (4,0,0), \quad \mu_k = (3,2,m_a), \quad \nu_k = (3,2,m_i).$$

Obviously, according to (16), both B_0 and B_1 involve s, d, and g components, and those naturally depend on the projections M_a and M_i of the atom's angular momentum:

$$B_0 = 0.113 Y_{00} - 0.031 \begin{bmatrix} 2 & 2 & 2 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 2 & 2 & 2 \\ \lambda & M_i & M_a \end{bmatrix} Y_{2\lambda},$$

$$B_1 = 0.080 Y - 0.206 \begin{bmatrix} 2 & 2 & 2 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 2 & 2 & 2 \\ \lambda & M_i & M_a \end{bmatrix} Y_{2\lambda}.$$

The coefficients of $Y_{4\lambda}$ turn out to be very small, and are not given here. For comparison, we point out[7] that the asymptotic wave function for the Sc atom contains only an s wave, and the corresponding coefficient obtained by boundary condition matching[7] is $B_0 = 1.11 Y_{00}$.

CONCLUSION

We have proposed a new way to find the asymptotic coefficients for multielectron atomic and ionic wave functions to an accuracy consistent with that of quantum-chemical calculations of the wave functions of those systems. This approach takes account of interelectron correlations and the contribution of different electron shells, automatically guaranteeing the correct Coulomb asymptotic radial and angular analytic dependence. Our calculations dealt specifically with light atoms and neglected fine structure, but relativistic corrections for heavy atoms can easily be incorporated. This would require substituting wave functions Ψ_a and ϕ_p into (12) and (15) that included spin-orbit coupling, which would also be included in the interaction potential V [Eq. (3)].

The asymptotic coefficients are universal characteristics of quantum systems, and are required for the solution of a variety of important physical problems. We plan to calculate these coefficients for other specific systems in the near future.

[1] E. L. Slaggi and E. H. Wichman, J. Math. Phys. 3, 946 (1962).
[2] R. Ahlrich, J. Math. Phys. 14, 1860 (1973).

[3] B. M. Smirnov, *Asymptotic Methods in Atomic Collision Theory* [in Russian], Atomizdat, Moscow (1973).

[4] R. Ahlrich, J. Chem. Phys. **54**, 2706 (1976).

[5] M. Hoffman-Ostenhof and T. Hoffman-Ostenhof, Phys. Rev. **A16**, 1782 (1977).

[6] J. Tal, Phys. Rev. **A18**, 1781 (1978).

[7] A. A. Radtsig and B. M. Smirnov, *Reference Data on Atoms, Molecules, and Ions*, Atomizdat, Moscow (1983) [updated version of Russian 1980 edition: Springer-Verlag, Berlin (1985)].

[8] G. K. Ivanov and M. A. Kozhushner, Fiz. Tverd. Tel. **20**, 9 (1978).

[9] G. K. Ivanov and M. A. Kozhushner, Khim. Fiz. **1**, 1039 (1982).

[10] G. K. Ivanov and M. A. Kozhushner, Chem. Phys. **170**, 303 (1993).

[11] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two-electron Atoms*, Springer-Verlag, Berlin (1957).

[12] M. G. Veselov, Opt. Spektrosk. **10**, 693 (1961).

[13] Y. Sakai and T. Anno, J. Chem. Phys. **60**, 620 (1974); J. Chem. Phys. **60**, 625 (1974).

[14] J. W. Richardson, W. C. Ninwpoort, R. R. Powell, and W. F. Edjell, J. Chem. Phys. **36**, 1057 (1962).

Translated by Marc Damashek