

Quasirelativistic formulation of the quantum-defect-orbital method

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The quantum-defect-orbital method has been reformulated in order to include a major part of the relativistic effects. The resulting quasirelativistic approach retains the simplicity of the original formulation but leads to more reliable results, particularly for the highly ionized atoms. The theory is illustrated by a series of calculations of oscillator strengths for the resonance transitions in atoms of lithium, sodium, and copper isoelectronic sequences.

I. INTRODUCTION

Quantum-defect theories, formulated in the 1950's by Ham¹ and Seaton,² have been, over the years, generalized³ and applied to describe complex atomic spectra,³⁻⁵ electron scattering,⁶ photoionization,⁷ and electron capture.⁸ A relativistic version of quantum-defect theory, constructed by Johnson and Cheng,⁹ was further generalized and applied, mainly to scattering phenomena, by Chang.¹⁰ In all these theories electrons are described by approximate eigenfunctions of an asymptotically correct Hamiltonian.

The quantum-defect-orbital (QDO) method has been proposed by Simons and Martin¹¹ to facilitate simple generation of atomic valence, Rydberg, and continuum orbitals from spectral data. The orbitals are referred to as quantum-defect orbitals (QDO's). Recently, the QDO method has also been applied under the name exact quantum-defect theory.¹² The QDO's are exact solutions of an eigenvalue equation of a model Hamiltonian and may be expressed in terms of the confluent hypergeometric functions. In consequence, expectation values of operators and transition integrals may be calculated analytically. The QDO method proved to be both simple and reliable. Therefore, it is a convenient tool for analyzing a large body of transition probability data¹³—in particular, in studying regularities in the behavior of the oscillator strengths along isoelectronic sequences,¹⁴ including two-electron transitions to doubly excited states¹⁵ and autoionizing resonances.¹⁶

There is abundant evidence indicating the importance of relativistic effects in highly ionized and in heavy atoms. However, the QDO formalism has originally been structured within the framework of the nonrelativistic (Schrödinger) theory and therefore it is inadequate to interpret transition probabilities and other properties of these systems. On the other hand, properties of highly ionized species are interesting not only from the formal point of view but are most important in physics of plasma and in astrophysics. The aim of this paper is to provide a relativistic formulation of the QDO method.

Relativistic atomic calculations, based on models rang-

ing from simple effective potential approaches to the Dirac-Hartree-Fock ones, have already been performed for all atoms of the periodic table. A nearly complete list of references may be found in a recent compilation by Pyykkö.¹⁷ Also, the corresponding computer programs are generally available.¹⁸ Nevertheless, it is still of some interest to develop new and simple atomic models, particularly if they are straightforward generalizations of the ones commonly used. In this paper we demonstrate that the nonrelativistic QDO radial equation is formally equivalent to the scalar relativistic (quasirelativistic) equation of Barthelat, Pelissier, and Durand¹⁹ and is closely related to a decoupled second-order Dirac equation.²⁰ In consequence, the QDO method, with practically no effort, may be reformulated in such a way that it takes into account most of the relativistic effects. This modification of the theory, on the one hand, does not add any complication to its formal structure and, on the other, creates a more solid background for its applications in interpreting properties of highly ionized atoms. In Sec. II the basic formalism is outlined. The Sec. III illustrates reliability of the method, taking as an example ions of the lithium, sodium, and copper isoelectronic sequences.

II. QUASIRELATIVISTIC FORMULATION

The second-order Dirac equation in a potential field $V(r)$, after the elimination of the spin and angular variables, may be written as²¹

$$\left(\Omega \underline{I} + \frac{\underline{M}}{r^2} \right) \begin{pmatrix} G_k \\ F_k \end{pmatrix} = 0, \quad (1)$$

where

$$\Omega = -\frac{d^2}{dr^2} + \frac{k^2}{r^2} + 2(V-E) - \alpha^2(V-E)^2 \quad (2)$$

and

$$\underline{M} = \begin{pmatrix} -k & -\alpha r^2 \frac{dV}{dr} \\ \alpha r^2 \frac{dV}{dr} & k \end{pmatrix}. \quad (3)$$

I is the 2×2 unit matrix, E is the difference between the total and the rest energy of the electron, and the other symbols have their usual meaning. For the quantum number k , we adopt the original convention of Dirac,²² i.e.,

$$k = \begin{cases} j + \frac{1}{2} = l + 1, & \text{if } j = l + \frac{1}{2} \\ -j - \frac{1}{2} = -l, & \text{if } j = l - \frac{1}{2} \end{cases} \quad (4)$$

In the case of a Coulomb potential,

$$V(r) = -\frac{Z}{r}, \quad (5)$$

where Z is the nuclear charge, a nonunitary transformation described by the matrix

$$\underline{A} = a \begin{pmatrix} 1 & -\frac{\alpha Z}{k+s} \\ -\frac{\alpha Z}{k+s} & 1 \end{pmatrix}, \quad (6)$$

where a is a constant and

$$s = k \left[1 - \frac{\alpha^2 Z^2}{k^2} \right]^{1/2}, \quad (7)$$

decouples the equations.^{19,20,23} The decoupled system of equations reads

$$\left[-\frac{d^2}{dr^2} + \frac{s(s \mp 1)}{r^2} - \frac{2Z(1 + \alpha^2 E)}{r} \right] \Phi_k^\mp = E(2 + \alpha^2 E) \Phi_k^\mp. \quad (8)$$

Its solution are related to the large and the small components of the Dirac wave functions as²⁰

$$\Phi_k^- = \frac{1}{2sa} [(k+s)G_k + \alpha Z F_k], \quad (9)$$

$$\Phi_k^+ = -\frac{1}{2|s|a} [\alpha Z G_k + (k+s)F_k]. \quad (10)$$

The constant a is determined from the normalization conditions

$$\langle G_k | G_k \rangle + \langle F_k | F_k \rangle = \langle \Phi_k^- | \Phi_k^- \rangle + \langle \Phi_k^+ | \Phi_k^+ \rangle = 1 \quad (11)$$

and is equal to

$$a = \frac{\bar{n}}{N|s|} \left[\frac{k(k+s)}{2} \right]^{1/2}, \quad (12)$$

where

$$\bar{n} = n - |k| + |s| \quad (13)$$

and

$$N = (\bar{n}^2 + \alpha^2 Z^2)^{1/2}, \quad (14)$$

with n being the principal quantum number of the nonrelativistic theory.

Equations (8) may be given two different interpretations. In the first, already discussed, this is a pair of

decoupled second-order Dirac equations. Their solutions are two components of the Dirac wave function. In the second interpretation, Eqs. (8) are two scalar equations for a scalar (quasirelativistic) wave function Ψ_k . Since the energy E does not depend upon the sign of k , we can set²⁰

$$\Phi_k^\pm = N_\pm \Psi_{\mp k}, \quad (15)$$

with

$$|N_\pm|^2 = \frac{k\bar{n} \mp sN}{2k\bar{n}} \quad (16)$$

chosen so that

$$\langle \Psi_k | \Psi_k \rangle = 1. \quad (17)$$

Denoting

$$Z' = Z(1 + \alpha^2 E) \quad (18)$$

and

$$e = E(1 + \frac{1}{2}\alpha^2 E), \quad (19)$$

we transform Eq. (8) into

$$\left[-\frac{d^2}{dr^2} + \frac{s(s-1)}{r^2} - \frac{2Z'}{r^2} \right] \Psi_k = 2e\Psi_k. \quad (20)$$

Equation (20) closely resembles the radial hydrogenic Schrödinger equation and passes into it in a trivial way in the nonrelativistic limit of $\alpha \rightarrow 0$. For the bound electron states

$$E = -\frac{Z^2}{N(N+\bar{n})}, \quad (21)$$

and Eqs. (18) and (19) may be rewritten, respectively, as

$$Z' = Z \frac{\bar{n}}{N}, \quad (22)$$

$$e = -\frac{(Z')^2}{2\bar{n}^2}. \quad (23)$$

Let us note that, according to Eqs. (7) and (13), $\bar{n} = n - \delta^0$, where

$$\delta^0 = |k| - |s| > 0 \quad (24)$$

is the noninteger part of $|s|$, since $|k|$ is the smallest integer that is larger than $|s|$. In the nonrelativistic case $\delta^0 = 0$.

The quantum-defect orbitals are solutions of the Schrödinger equation¹¹

$$\left[-\frac{d^2}{dr^2} + \frac{\lambda(\lambda+1)}{r^2} - \frac{2Z_{\text{net}}}{r^2} \right] \Psi_k^{\text{QD}} = 2E^{\text{QD}} \Psi_k^{\text{QD}}, \quad (25)$$

where Z_{net} is the nuclear charge seen by the electron at large r and

$$\lambda = l - \delta + c, \quad (26)$$

where δ is the quantum defect and c is an integer chosen to ensure the correct number of nodes and normalizability.

ty to Ψ^{QD} . The eigenvalue E^{QD} in Eq. (25) depends only upon the noninteger part of λ and, hence, it is independent of c . The quantum defect is obtained empirically from the following equation:

$$E^{\text{QD}} = E^X = -\frac{Z_{\text{net}}^2}{2(n-\delta)^2}, \quad (27)$$

where E^X is the experimental energy. A comparison of Eqs. (25) and (20) as well as (27) and (23) demonstrates that the formal mathematical structures of the QDO theory and of the scalar relativistic theory are the same. This formal similarity allows us to reinterpret the QDO theory so that it accounts for a major part of relativistic effects.

The relativistic quantum-defect-orbital (RQDO) equation may be written as

$$\left[-\frac{d^2}{dr^2} + \frac{\Lambda(\Lambda+1)}{r^2} - \frac{2Z'_{\text{net}}}{r^2} \right] \Psi_k^{\text{RD}} = 2e^{\text{RD}} \Psi_k^{\text{RD}}, \quad (28)$$

where

$$\Lambda = \begin{cases} s-1-\delta'+c & \text{if } j=l+\frac{1}{2} \\ -s-\delta'+c & \text{if } j=l-\frac{1}{2} \end{cases} \quad (29)$$

and

$$Z'_{\text{net}} = Z_{\text{net}}(1+\alpha^2 E^X). \quad (30)$$

Similarly to the nonrelativistic case, the relativistic quantum defect δ' is determined empirically. We have

$$e^{\text{RD}} = -\frac{(Z'_{\text{net}})^2}{2(\bar{n}-\delta')^2} \quad (31)$$

and, taking into account Eqs. (19), (30), and (31), the value of δ' is obtained from

$$\frac{E^X(1+\frac{1}{2}\alpha^2 E^X)}{(1+\alpha^2 E^X)^2} = -\frac{Z_{\text{net}}^2}{2(\bar{n}-\delta')^2}. \quad (32)$$

Let us compare QDO's obtained as solutions of the nonrelativistic Eq. (25) and the relativistic Eq. (28). Both the equations are formally the same and the corresponding orbitals may be, in both cases, expressed in terms of generalized Laguerre polynomials. Their functional form and properties were already discussed in detail by several authors.^{11,19} Also, expressions for the transition integrals and expectation values of various operators were published.^{11,19,24} The wave functions in the nonrelativistic/relativistic case are determined by two parameters: λ/Λ and $E^{\text{QD}}/e^{\text{RD}}$. The first of these parameters is responsible for behavior of the wave function if $r \rightarrow 0$ and the second one if $r \rightarrow \infty$. At the origin,

$$\frac{1}{r} \Psi^{\text{QD}}(r) \sim r^\lambda \quad (33)$$

and

$$\frac{1}{r} \Psi^{\text{RD}}(r) \sim r^\Lambda. \quad (34)$$

Comparing Eqs. (27) and (32), we see that

$$\frac{\bar{n}-\delta'}{n-\delta} = 1 + \frac{3}{4}\alpha^2 E^X + O(\alpha^4) \quad (35)$$

or, considering again Eqs. (27) and (13),

$$\delta - \delta' = |k| - |s| - \frac{3}{8} \frac{\alpha^2 Z_{\text{net}}^2}{n-\delta} + O(\alpha^4); \quad (36)$$

In the case of relativistic hydrogenic wave functions, s determines their behavior near the origin. Therefore, we assume that s is determined by the unscreened value of Z rather than by Z_{net} .²⁵ Hence,

$$\delta - \delta' = \frac{\alpha^2 Z^2}{2|k|} \left[1 - \frac{3}{4} \frac{Z_{\text{net}}^2}{Z^2} \frac{|k|}{n-\delta} \right] + O(\alpha^4). \quad (37)$$

Now, using Eqs. (29), (26), and (4), we get

$$\Lambda = \lambda - \frac{3}{8} \frac{\alpha^2 Z_{\text{net}}^2}{n-\delta} + O(\alpha^4). \quad (38)$$

For the S -type orbitals, $l=0$ and $\lambda = -\delta + c$. If $c=0$, i.e., if the QDO's possess the same number of nodes as their hydrogenic counterparts, then both $\lambda < 0$ and $\Lambda < 0$, i.e., both nonrelativistic and relativistic wave functions, are singular at the origin, the relativistic singularity being stronger. The wave functions are quadratically integrable providing that $\Lambda > -\frac{3}{2}$. This means that for $j = \frac{1}{2}$ states the nonrelativistic condition $\delta < \frac{3}{2}$ is replaced by

$$\delta' < \frac{3}{2} - \frac{1}{2}\alpha^2 Z^2, \quad (39)$$

the last relation being a straightforward consequence of Eq. (29). For $r \rightarrow \infty$,

$$\Psi^{\text{QD}}(r) \sim \exp[-r(-2E^{\text{QD}})^{1/2}], \quad (40)$$

$$\Psi^{\text{RD}}(r) \sim \exp[-r(-2e^{\text{RD}})^{1/2}]. \quad (41)$$

These asymptotic behaviors are exactly the same as the ones of the exact solutions (corresponding to the eigenvalue E^X) of the Schrödinger and Dirac equations, respectively.

In the present formulation, the relativistic QDO's are one-component functions. Therefore, this theory is quasirelativistic and any comparison with the multicomponent relativistic Dirac-Fock formulation should be performed using electron densities rather than wave functions. A detailed comparison between the quasirelativistic and relativistic theories may be found in the literature.^{19,20} The conclusion is that the quasirelativistic formulation allows for obtaining about 90% of the relativistic corrections to energies, transition probabilities, and expectation values of powers of r . From the present analysis we can see that the relativistic density distribution approximates very well the exact one for large values of r [Eq. (41)]. At small distances the quality of the densi-

TABLE I. Oscillator strengths (multiplied by 10^3) for the resonance transition $(ns)^2S \rightarrow (np)^2P$ in Li, and Cu isoelectronic sequences calculated using the nonrelativistic quantum-defect-orbital method (QDO) and its relativistic modification (RQDO), compared with the Dirac-Hartree-Fock (DHF) and experimental values.

Z	Ion	Upper level	QDO	RQDO	DHF	Expt.
Lithium sequence						
36	Kr ³³⁺	2P _{1/2}	21	13	13 ^a	
		2P _{3/2}	42	50	50 ^a	
42	Mo ³⁹⁺	2P _{1/2}	23	11	11 ^a	
		2P _{3/2}	45	57	56 ^a	
48	Cd ⁴⁵⁺	2P _{1/2}	25	10	10 ^a	
		2P _{3/2}	50	66	64 ^a	
54	Xe ⁵¹⁺	2P _{1/2}	29	9	8 ^a	
		2P _{3/2}	57	77	75 ^a	
59	Pr ⁵⁶⁺	2P _{1/2}	32	9	8 ^a	
		2P _{3/2}	65	89	86 ^a	
Sodium sequence						
26	Fe ¹⁵⁺	3P _{1/2}	134	127	125 ^b	
		3P _{3/2}	268	275	272 ^b	
36	Kr ²⁵⁺	3P _{1/2}	102	87	87 ^b	
		3P _{3/2}	204	218	216 ^b	
42	Mo ³¹⁺	3P _{1/2}	94	74	73 ^b	
		3P _{3/2}	188	207	206 ^b	
54	Xe ⁴³⁺	3P _{1/2}	91	56	56 ^b	
		3P _{3/2}	182	217	215 ^b	
74	W ⁶³⁺	3P _{1/2}	113	42	41 ^b	
		3P _{3/2}	226	297	289 ^b	
Copper sequence						
42	Mo ¹³⁺	4P _{1/2}	243	223	232 ^c	230±20 ^d
		4P _{3/2}	486	506	531 ^c	530±40 ^d
53	I ²⁴⁺	4P _{1/2}	209	172	177 ^e	190±8 ^f
		4P _{3/2}	419	455	476 ^e	439±19 ^f
74	W ⁴⁵⁺	4P _{1/2}	204	119	122 ^e	
		4P _{3/2}	408	489	515 ^e	
79	Au ⁵⁰⁺	4P _{1/2}	210	111	114 ^e	
		4P _{3/2}	421	515	544 ^e	
82	Pb ⁵³⁺	4P _{1/2}	215	107	109 ^e	
		4P _{3/2}	431	534	564 ^e	

^aCheng, Kim, and Desclaux, Ref. 26.

^bCheng and Kim, Ref. 27.

^cCheng and Kim, Ref. 28.

^dBeam-foil experiment results taken from Ref. 29.

^eInterpolated from results of Ref. 28.

^fBeam-foil experiment results taken from Ref. 30.

ty deteriorates [Eqs. (34) and (38)]. This behavior is very similar to that of the nonrelativistic QDO densities when they are compared to the exact nonrelativistic ones.¹¹

The most important difference between the RQDO and QDO equations is the explicit dependence of the former one on the total angular momentum quantum number k . In consequence, in the relativistic formulation, values of δ' are determined by the fine-structure splitted energies rather than by their centers of gravity. The corresponding relativistic QDO's are different for each component of the multiplet and, if $c=0$, they retain the nodal structure of large components of the hydrogenic Dirac wave functions.

III. NUMERICAL ILLUSTRATION

Solutions of Eqs. (25) and (28) have the same functional form. As a consequence, all radial integrals may be calculated using the same algorithms and the same computer programs as in the case of the nonrelativistic QDO method. Therefore, we do not reproduce here the corresponding equations and refer the reader to earlier papers.¹¹ In order to perform a RQDO calculation, it is sufficient to replace in the input data λ by Λ and Z_{net} by $Z_{\text{net}}(1+\alpha^2 E^X)$. A comparison of the oscillator strengths for the resonance transitions $(ns)^2S \rightarrow (np)^2P$ in the lithium ($n=2$), sodium ($n=3$), and copper ($n=4$) isoelectronic sequences calculated through the QDO and RQDO methods with theoretical and/or experimental data is given in Table I. We can see two advantages of the relativistic formulation. First, we can interpret correctly the fine-structure splittings. Second, in the cases where relativistic effects are noticeable, the agreement between the calculated and observed (or reliable theoretical) values of the oscillator strengths is considerably better in this formulation.

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