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Comment on "Analytical wave functions for atomic quantum-defect theory"

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The atomic quantum-defect theory proposed by Kostelecký and Nieto [Phys. Rev. A **32**, 3243 (1985)] is proven to be basically identical to the earlier published quantum-defect orbital formalism.

In Ref. 1, Kostelecký and Nieto present an exactly solvable potential that reproduces atomic spectra in the so-called limit of quantum defect theory, i.e., the limit in which the principal quantum number n is modified by a constant quantum defect, $n^*=n-\delta(l)$, for a fixed value of l, the angular-momentum quantum number.

The aforementioned effective potential is chosen to satisfy, according to Eq. (9) of Ref. 1,

$$\frac{l(l+1)}{y^2}+V_{\text{eff}}(y)=\frac{l^*(l^*+1)}{y^2}\ , \tag{1}$$

where $y=\beta r$ ($\beta=2/a_0$) and l^* is defined as follows:

$$l^*=l-\delta(l)+I(l)\ , \tag{2}$$

$\delta(l)$ being, as noted above, the quantum defect for a given Rydberg series characterized by the angular momentum quantum number l. The quantum defect for each atomic state is related to the energy eigenvalue through the expression

$$E_{n^*}=-\frac{E_0}{n^{*2}}=-\frac{E_0}{[n-\delta(l)]^2}\ , \tag{3}$$

where E_0 is the Rydberg constant and n^* is generally known as the effective principal quantum number. At this point, a somewhat misleading remark, in our view, is introduced by the authors in Ref. 1. They state that $\delta(l)$ is approximately constant for a given l, $l\geq 0$, that is, for a given Rydberg series. In reviewing quantum defects in the literature (e.g., Kuhn,[2] whose reported quantum defects have been employed by Kostelecký and Nieto in Ref. 1) we find that for the low-lying levels of some Rydberg series with small values of l the quantum defect changes appreciably. For instance, in the $np\ ^2P$ series of lithium, the quantum defect varies from 0.034 in the $2p$ level to 0.044 in the $3p$ level and then it takes the constant value of 0.050 for the remaining np ($n>3$) levels. The use of the asymptotic quantum defect for an entire Rydberg series, as done in Ref. 1, leads to incorrect results for transition probabilities when the transitions involve low-lying levels, especially in the results reported in Ref. 1 for sodium, as the authors acknowledge in the analysis of their results.

In Eq. (2) $I(\delta)$ is an integer whose allowed range of values is determined, in each case, in such a way that the kinetic and potential energies are separately normalizable and that the radial functions have a positive (or zero) number of nodes.

In proposing this procedure, the authors in Ref. 1 have overlooked several publications, in particular Refs. 3 and 4, where, as early as in 1974 and 1975, the following model potential, within the quantum-defect orbital (QDO) formalism, was proposed:

$$V(r)=\frac{\lambda(\lambda+1)-l(l+1)}{2r^2}-\frac{Z_{\text{net}}}{r}\ , \tag{4}$$

where the atomic units employed are hartrees. Z_{net} is the effective nuclear charge at large radial distances ($Z_{\text{net}}=Z-N+1$ for an N-electron atomic system with atomic number Z, i.e., $Z_{\text{net}}=1$ for a neutral atom), and λ is a parameter defined as follows:

$$\lambda=l-\delta+c\ . \tag{5}$$

In Eq. (5) l and δ have the same physical meaning as the symbols in Eq. (2), and c was originally defined as "any" integer although with clear suggestions as to the criteria to follow for its choice, i.e., that the effective centrifugal barrier be close to the actual barrier and that the number of nodes in the radial function be close to that in the exact function. In the first two QDO papers[3,4] c was in most cases taken to be the rounded integer nearest to the quantum defect, that is, Int(δ).

When Eq. (4) is substituted into the central field radial equation, the following is obtained:

$$-\frac{1}{2}\frac{d^2\mu(r)}{dr^2}+\left[\frac{\lambda(\lambda+1)}{2r^2}-\frac{Z_{\text{net}}}{r}\right]\mu(r)=E\mu(r)\ , \tag{6}$$

where $\mu(r)$ is the radial part of the wave function multiplied by r. This radial wave equation can be proven to be identical to that obtained with the effective potential of Ref. 1, Eq. (1) above, the slight differences in notation being taken into account. Kostelecký and Nieto only seem to consider neutral atoms, and therefore instead of Z_{net} they always write 1.

The radial solutions of the wave equation in Ref. 1 are written in terms of associated Laguerre polynomials. Once normalized they are as follows [Eq. (11) in Ref. 1]:

$$R_{n^*l^*}(y)=(n^*)^{-2}[\beta^3\Gamma(n-l-I)/2\,\Gamma(n^*+l^*+1)]^{1/2}\times(y/n^*)^{l^*}e^{-y/2n^*}L_{n-l-I-1}^{(2l^*+1)}(y/n^*)\ . \tag{7}$$

Equation (13) of Simons,[3] gives the following normalized $\mu(r)$ solutions to Eq. (6) above for the case in which $c=\text{Int}(\delta)$ (but which may be written as c more generally):

$$\mu(r)=\left[\frac{2Z_{\text{net}}}{n-\delta}\right]^{l+3/2-\delta+\text{Int}(\delta)}\left[\frac{(n-l-1-\text{Int}(\delta))!}{2(n-\delta)\Gamma(n+l+1+2\delta+\text{Int}(\delta))}\right]^{1/2} r^{\lambda+1}e^{-Z_{\text{net}}r/(n-\delta)}L_{n-l-1-\text{Int}(\delta)}^{(2\lambda+1)}\left[\frac{2Z_{\text{net}}r}{n-\delta}\right]. \tag{8}$$

The functions in Eq. (8) are proven to be, after very straightforward algebra, identical with those of Eq. (7) multiplied by r if atomic units are consistently used throughout and β is simply taken as 2.

Kostelecký and Nieto, who gave in (1) an analytical expression for the expectation values of $y^d=(\beta r)^d$ in the transitions from the level (n_i,l_i) to the level (n_f,l_f) [Eq. (13) of Ref. 1], claim that their "use of analytical wave functions to calculate transition probabilities seems to be new," whereas in Refs. 3 and 5 exactly the same analytical expression as their Eq. (13) for $d=1$ had been published a decade earlier. Also, in 1977 and 1980, respectively, other authors employed the quantum defect orbitals to obtain an analytical expression for the dynamic polarizability (6) and to carry out a unified treatment of oscillator strengths and multipole polarizabilities of the QDO, Coulomb approximation, and the extended Coulomb approximation methods.[7]

We therefore find no justification for calling the model potential (1) a "new model potential." Regardless of the very minor peculiarities in Kostelecký and Nieto's and the QDO procedures, it seems clear that the quantum defect theory proposed in Ref. 1 and later quoted by the same authors[8] is essentially the same as the quantum defect orbital formalism. Some remarks that support our view have been very recently found in the literature.[9] Other works by the authors of this Comment involving the QDO formalism and some extensions of it have appeared in the literature from 1985–1990.[10–18]

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