

Comment on "Fine structure and analytical quantum-defect wave functions"

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It is pointed out that the valence-electron Schrödinger equation used by Kostecký, Nieto, and Truax [Phys. Rev. A 38, 4413 (1988)] had already been presented and studied by Simons [J. Chem. Phys. 55, 756 (1971)], and it is shown that expectation values calculated using its eigenfunctions are unreliable.

In Ref. 1, Kostecký, Nieto, and Truax "investigate the domain of validity" of analytical wave functions for alkali-metal and singly ionized alkaline-earth-metal valence electrons obtained from the exact solution of a Schrödinger equation developed and used in some earlier papers.²⁻⁴ The object of this Comment is to point out that their equation is identical to that presented by Simons⁵ in 1971 based upon what Simons called the "atomic Fues potential," and that the raw wave functions from the treatment are intrinsically unreliable for the calculation of expectation values.

The exactly soluble Schrödinger equation given by Kostecký, Nieto, and Truax is one for which the potential-energy function for the valence electron when written in Hartree atomic units is of the form

$$V(r) = -\frac{Z}{r} + \frac{l^*(l^* + 1) - l(l + 1)}{r^2}, \quad (1)$$

where Z is the charge on the core. The definition of l^* that they give is such that the energy eigenvalues of the Schrödinger equation are the observed Rydberg terms

$$E(n, l) = -\frac{E_0}{n^{*2}}, \quad (2)$$

where

$$n^* = n - \delta(l), \quad (3)$$

and E_0 is a constant.

Simons introduced his equation within the context of model pseudopotential approaches. The model potential for his equation was given by

$$V(r) = -\frac{Z}{r} + \sum_{l=0}^{\infty} \frac{B_l \hat{P}_l}{r^2}, \quad (4)$$

where \hat{P}_l is a projection operator projecting out spherical harmonics of a given value of l . Exact solution of the Schrödinger equation yielded energy eigenvalues given by

$$E = -2Z^2 / \{2P + 1 + [(2l + 1)^2 + 8B_l]^{1/2}\}^2 \\ P = 0, 1, 2, \dots \quad (5)$$

The B_l 's were fit to the lowest observed energies of each value of l . It will be noted that Eq. (4) is just another way

of writing the Rydberg formula. Thus there is a one-to-one correspondence between the equations and solutions of Simons and those of Kostecký, Nieto, and Truax. Simons applied his approach to the alkali metals, the singly ionized alkaline-earth metals, and the unionized alkaline-earth metals. The pseudopotentials obtained have also been used in molecular calculations.^{6,7}

The unreliability of expectation values obtained using the above solutions has been vividly displayed in a paper by Goodfriend.⁸ In that paper it was shown that one can apply the pseudopotential formalism to excited states of the hydrogen atom, considering an electron in an excited state as a valence electron and the unoccupied lower states as a core. The pseudo-Hamiltonian for the "valence" electron can then be written

$$\hat{H} = -\frac{\nabla^2}{2} - \frac{1}{r} + \sum_{l < n} \frac{[n(n-1) - l(l+1)]}{2r^2} \hat{P}_l, \quad (6)$$

which is in the Simons form. The energy eigenvalues are then

$$E = -\frac{1}{2}(P + n)^2, \quad P = 0, 1, 2, \dots \quad (7)$$

Examination of Eq. (7) shows that if we choose a value for n , representing the excited state considered the "valence" orbital, then Eq. (7) yields the exact energies for that state and all higher states. However, the expectation value of the kinetic energy for $P=0$ is given by

$$\langle \hat{T} \rangle = \frac{1}{2n^2} - \frac{[n(n-1) - l(l+1)]}{n^3(2n-1)}. \quad (8)$$

The exact value for that state is

$$\langle \hat{T} \rangle = 1/2n^2. \quad (9)$$

Thus the potential energy must also be wrong. With respect to spatial expectation values, $\langle 1/r \rangle$ is correctly calculated, but for $\langle 1/r^2 \rangle$ for $P=0$,

$$\langle 1/r^2 \rangle = 2/n^3(2n-1). \quad (10)$$

The exact hydrogen result is

$$\langle 1/r^2 \rangle = 2/n^3(2l+1). \quad (11)$$

In the case where $n = l + 1$, they agree, but this is just the

condition for the problem to reduce to the conventional hydrogen problem.

This problem with the calculation of expectation values and matrix elements is a general one for pseudopo-

tential treatments. A prescription for correcting such wave functions so that properties can be calculated from them has been presented by Daasch, McMurchie, and Davidson.⁹

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