Further comments on atomic central-potential models*

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The Hartree-Slater (HS) and Green-Sellin-Zachor (GSZ) model atomic potentials are compared. Results of various calculations based upon these potentials show the HS to be decidedly more realistic in diverse physical situations.

I. INTRODUCTION

A recent comment[1] argues that the atomic central field model of Green, Sellin, and Zachor[2] (GSZ) is superior to the Hartree-Slater model of Herman and Skillman[3] (HS). This is an important question because, although computational schemes for very accurate atomic wave functions are available,[4,5] they are not used for large-scale survey calculations of atomic properties because they are cumbersome and time consuming. Central potential models are thus an attractive alternative owing to their simplicity, speed, and their proven ability to predict quantitatively diverse physical properties.[6-20]

The rigorous formulation of atomic theory involves a noncentral, nonlocal many-body potential. This potential cannot be approximated in *all* regions of the configuration space by a given central potential since the noncentral many-body aspects of the exact potential are not small. For example, a central potential which gives good dipole moments might be quite poor for hyperfine structure calculations. Thus, agreement between experimental values of a given property with the results of a central-potential model calculation does *not* imply that agreement would be found for other properties, a fact which is also well-known in nuclear physics.[21] This is because the major contributions to the matrix element for different properties comes from different regions of the configuration space and the relative accuracy of the central potentials must differ in these regions as well.

It has been argued[1] that the GSZ potential is "better" for *all* atomic properties involving valence electrons than the HS potential because the former "predicts" more accurate energies for the ground state and valence-shell excitations. The discussion of the previous paragraph shows the flaw of this line of reasoning. In addition, this is really circular reasoning because the GSZ potential is obtained by fitting to the energies of the ground state and valence-shell excitations so that this agreement is not an *a priori* prediction, but rather a constraint on the potential.

The critical comparison, then, is a calculation of various atomic properties employing each potential and comparing the results with measured values or more accurate calculations such as Hartree-Fock (HF). In this way, one can decide which central potential is more accurate for the given property. Fortunately, many calculations appear in the literature using both the HS potential and the GSZ potential. In the next section, we compare some of these results with each other and experiment or HF results.

II. COMPARISONS OF ACCURACY OF HS AND GSZ RESULTS

As a first comparison, we consider the asymptotic quantum defects (equivalently zero-energy phase shifts) for the noble gases Ne, Ar, Kr, and Xe. Table I gives the GSZ results[22] and the HS results[18,23] and they are compared with the HF results for excitation of an outer s or p electron in an optical ^1P channel.[23] The striking thing about these results is that for s, p, or d waves $\delta_l^{GSZ}(0)$

TABLE I. Asymptotic quantum defects (zero-energy phase shifts in units of π) for $l = 0, 1, 2$ in the noble gases. The GSZ results are from Ref. 22, the HS results from Refs. 18 and 23, and the HF ^1P results from Ref. 23.

	Ne			Ar			Kr			Xe		
l	GSZ	HS	HF	GSZ	HS	HF	GSZ	HS	HF	GSZ	HS	HF
0	1.33	1.28	1.27	2.19	2.08	2.06	3.16	3.02	3.02	4.11	3.91	3.88
1	0.86	0.80	0.80	1.73	1.62	1.61	2.68	2.55	2.53	3.61	3.49	3.44
2	0.01	0.00	0.00	0.21	0.10	0.02	1.27	1.11	1.00	2.42	2.21	2.00

$> \delta_l^{HS}(0) \geq \delta_l^{HF(^1P)}(0)$ in every case. Moreover, $\delta_l^{HS}(0)$ is often quite close to $\delta_l^{HF(^1P)}(0)$. The fact that the GSZ phase shifts are too large means that the GSZ potential is too attractive, particularly near the outer edge.

The next point concerns the outer region of the potential itself. It is well-known that the effective potential for d and f waves are often composed of an inner well and an outer well separated by a potential barrier.[23-27] The details of this barrier are quite important for atomic properties involving d or f states. Such a barrier exists for the d-wave effective potential in argon. The GSZ and HS results for the outer region of the potential are shown in Fig. 1, where it is seen that the HS potential shows a barrier while the GSZ does not. From the phase-shift relations of Table I it is seen that the lack of a barrier clearly exemplifies our observations that the GSZ potential is too attractive. The HF phase shifts are still smaller than the HS, indicating that the "true" barrier[28] is even higher than that predicted by the HS potential, and is certainly not absent as the GSZ potential predicts. The fact that the photoionization cross section for argon $3p$ is *increasing* from threshold experimentally,[23] in the HF approximation,[23] and in the HS approximation,[7] but *decreasing* in the GSZ approximation,[29] is a further indication that the GSZ potential is too attractive in the valence-shell region.

The comparison of threshold photoionization cross sections[7,23,29] for Ar, Kr, and Xe is given in Table II. The experimental results[30] are roughly in a ratio of 1:2:3 as are the HS results. The HS results are, however, a factor of 2 too large, owing to the fact that the d-wave barrier is somewhat too small (as discussed above) so that the continuum d wave at threshold is too penetrating. The GSZ results are essentially constant and therefore sharply contradictory to experiment, as can be seen from the Table.

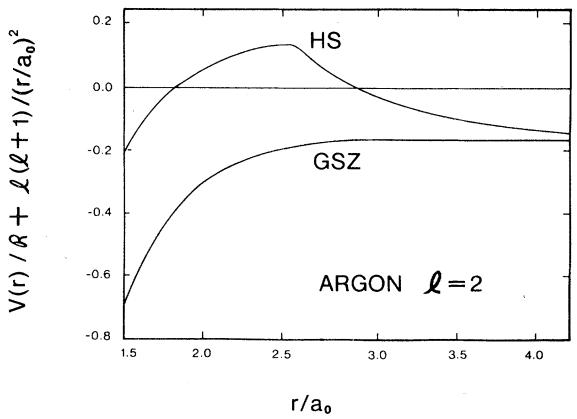

FIG. 1. Argon d-wave ($l=2$) potential in the vicinity of the outer edge of the atom. The GSZ result is from Ref. 22 and the HS from Refs. 7 and 24.

TABLE II. Threshold photoionization cross sections for Ar, Kr, and Xe (in units of megabarns) showing GSZ results (Ref. 29), HS results (Refs. 7 and 23), and experiment (Ref. 30). The GSZ results could be read only approximately from a log plot.

	GSZ	HS	Expt
Ar	~80	45.1	20.1
Kr	~80	79.6	42.0
Xe	~80	124.7	60.0

Finally, we note that the GSZ potential obtained by fitting to valence excitations is relevant only to outer subshells.[1,22] In contrast, the HS potential has been shown in a large number of cases to be quite good for inner-shell atomic properties including photoionization,[7,9-11,13] Auger transition rates,[12,13] x-ray transition rates,[10] charged-particle impact ionization,[14,15] as well as others.[18,19,27,31,32]

III. CONCLUDING REMARKS

Predictions of calculations based upon GSZ and HS potentials have been compared above and the HS has been found to be more realistic in these cases. Thus, the claim of Ref. 1 that GSZ is inherently better is without foundation. From the comparisons which we have presented, however, one might draw just the opposite conclusion. Fitting potentials better to energy levels (as is done in the GSZ case) and then claiming that the potential is better because it "predicts" energies better is a circular argument; the claim is not only unconvincing, but also incorrect. The introduction of the Latter cutoff[33] in the HS potential as a means of subtracting off the "self-potential" is focussed upon in Ref. 1 as the "flaw" in the HS method. While this cutoff is a bit arbitrary, the fact that the HS potential is indeed more realistic than GSZ near the outer edge of the atom implies that much of the physics of the situation is preserved with the Latter cutoff.

Finally, we note that central-potential wave functions are often used as an initial approximation (or basis set) upon which successively improved approximations, such as many-body perturbation theory or continuum configuration interaction, are based. In principle, any complete basis set could be used. It is strongly desirable, however, to use an initial approximation which is assessible, i.e.,

it is important to know precisely what physics is contained in the initial approximation. The HS potential, since it results from an *ab initio* calculation, provides such an initial approximation. The *semi-empirical* GSZ potential does not since it includes unknown amounts of exchange, correlation, and relativistic effects.

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[28]Strictly speaking the HF calculation involves a nonlocal potential and one cannot speak of a barrier as if it were a central potential. We can, however, define an "effective" central potential for zero energy continuum electrons as $V_{\text{eff}}(r) = (\hbar^2/2m)P''_{\varepsilon l}/P_{\varepsilon l}$ and thus get some idea of whether or not the potential is positive or negative in a given region ($P_{\varepsilon l}$ is the continuum HF wave function). Using the results of Ref. 23 we then get some information of the "true" barrier. This, of course, breaks down for $P_{\varepsilon l} = 0$.

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