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Reply to "Further comments on atomic central-potential models"

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We indicate a weakness in the Hartree-Fock-Slater-Latter (HFSL) potential at values of r near the point where the Latter hydrogen-potential addition is made. The GSZ (Green-Sellin-Zachor) potential does not have this weakness and, consequently, can yield energy eigenvalues which are closer to experimental energy levels than are the HFSL energy eigenvalues. We attempt to show that the examples used in Manson and Purcell's Comment fail to demonstrate that the HFSL potential is more accurate than the GSZ potential. We suggest possible avenues along which further development of atomic independent-particle models might proceed.

I. INTRODUCTION

We agree with Manson and Purcell[1] (MP) that no central potential can approximate the actual atomic potential in all regions of the atom. One of the points of our earlier Comment[2] (to be referred to as DGG) is that the Hartree-Fock-Slater-Latter (HFSL) potential of Herman and Skillman[3] is particularly poor in its approximation of the potential encountered by valence-state electrons. We suggested two related reasons for this problem. First, the large-r behavior of the HFSL potential does not arise in a natural or *a priori* manner since the Latter device is employed to substitute a $-2/r$ potential for the Hartree-Fock-Slater (HFS) potential at all values of r where the magnitude of the HFS potential is less than $2/r$. Secondly, we presented evidence, the experimental valence and excited-state energy levels, which suggests that the value of r where the Latter substitution is first made is too small and results in a potential which is usually less attractive than the optimum independent particle model (IPM) potential.

In our earlier Comment, we showed that the IPM potential of Green, Sellin, and Zachor[4] (GSZ), with the form

$$V(r) = -2[(Z-1)\Omega(r)+1]/r, \tag{1}$$

where

$$\Omega(r) = [H(e^{r/d}-1)+1]^{-1}, \tag{2}$$

is capable of yielding energy eigenvalues which are much closer to experimental energy levels than are the corresponding eigenvalues associated with the HFSL potential. The fact that the two parameters, H and d, of the GSZ potential are adjusted to fit the GSZ energy eigenvalues to experimental energy levels does not detract from the significance of the fact that a large number of GSZ eigenvalues are more accurate than the corresponding HFSL eigenvalues. One could not choose any arbitrary two-parameter potential with incorrect or abruptly changing asymptotic behavior and expect it to yield accurate valence-state energy eigenvalues. We maintain that, in the vicinity of the value of r where the Latter substitution is made in the HFSL potential, the behavior and magnitude of the GSZ potential is more realistic than is the HFSL potential.

II. COMPARISONS BETWEEN GSZ AND HFSL

Again, we agree with MP that the fact that an IPM potential yields one particular atomic property accurately does not mean that potential will accurately yield a different atomic property. To best compare the accuracy of two different IPM potentials, one should consider a wide range of relevant atomic properties for atoms having a wide range of electronic configurations. Unfortunately, MP have chosen to consider only noble gases in their comment. Nevertheless, we are glad to examine the examples they have put forward.

In comparisons of quantum defects (or zero-energy phase shifts in units of π) MP note that $\delta_{l\,\mathrm{GSZ}}(0) > \delta_{l\,\mathrm{HS}}(0) > \delta_{l\,\mathrm{HF}}^{(^1P)}(0)$ for s, p, or d waves for all four noble gases considered. In view of the direct relationship between quantum defects and energy eigenvalues, this fact is simply another way of saying that the GSZ energy eigenvalues are in closer agreement with experimental energy levels than are HFSL or Hartree-Fock eigenvalues. Since we maintain that the accuracy of an atomic potential is best assessed by determining how well the atomic properties it yields agree *with experiment* and not how well they agree with Hartree-Fock theory, we feel this example cited by MP only reinforces the discussion in DGG.

In their second example, MP claim that there exists a potential barrier at intermediate r for the d state of Ar, whereas GSZ does not predict a barrier in this case. Since the presence or absence of a d- or f-state barrier depends very sensitively upon differences in magnitude between two large quantities, i.e., the negative IPM potential and the positive centrifugal potential, general claims such as those made in MP should be made on the basis of many examples rather than a single example which might be an exception to the general rule. Even for this one example, it is not clear whether sophisticated Hartree-Fock-Rothaan (HFR)[5] calculations would imply the existence of such a barrier since the HFR valence-state eigenvalue of Ar is -1.182 Ry. The experimental value is -1.1580 Ry, while GSZ adjusts to -1.1587 Ry, and HS yields -1.0613 Ry. This would suggest that the reason HS predicts a d-state potential barrier relates directly to the weakness of the HS potential in the valence-shell region so that the d-state centrifugal potential prevails in the difference at some intermediate value of r. It is interesting to observe that Fig. 1 of Ref. 1 shows this barrier peaks at $r = 2.6a_0$ which is the value of r where the Latter substitution is made in the HFSL potential. Despite an intensive search in the five general references on this subject given by MP we have not found any concrete *experimental* evidence pointing unequivocally to the existence of a d-state barrier in argon.

From the discussion by Fano[6] (Ref. 26 of MP), it should be clear that these barriers manifest themselves in a variety of unexpected ways. In effect, the small difference between the potential and the centrifugal barrier depends sensitively "on such poorly predictable details as exchange and correlations." Fano mentions that inner vacancies and the physical-chemical environment of the atom may also play a role in establishing such potential barriers. An analogous situation arises in the nuclear force problem[7,8] where the approximate cancellation of the large attractive potential arising out of the exchange of an isoscalar scalar meson (ϵ) is approximately cancelled by the large repulsive potential arising out of the exchange of an isoscalar vector meson (ω). The resulting difference is then very sensitive to spin, velocity-dependent, nonlocal, and other complex two-body interaction components which are comparatively small on the scale of the static potentials themselves. As suggested by Fano[6] we need new experimental and theoretical approaches to establish the physical meaning of the residuals near weak atomic barriers.

In the MP discussion on photoionization cross sections at threshold, the authors cite results drawn from Berg and Green[9] in which the reader was cautioned that the krypton and xenon results are suspect because only a limited number of partial waves were considered. Assuming, nevertheless, that we accept the GSZ values given by MP, it should be noted that they are as good or better than the HSFL values on a percentage basis in two of the three cases cited.

In addition to these three numerical comparisons, MP also say that the *ab initio* character of the HSFL potential makes it more attractive to use in generating wave functions to serve as a basis set in starting a more sophisticated calculation because it is "important to know precisely what physics is contained in an initial approximation." Unfortunately, work[10,11] in the years following Herman and Skillman's calculations has indicated that the coefficient of the Slater approximation to the exchange interaction should not be unity as in the HFSL program but rather 2/3,[12] or else an adjustable constant (α).[13,14] Furthermore, in view of the nonphysical vanishing of the true HFS potential at large r necessitating the *ad hoc* Latter device, it seems to us that the exact nature of the physics in the HFSL potential is not readily apparent. The MP characterization of the Latter device as a "cutoff" seems misleading since in reality the Latter device "adds on" a hydrogen potential to the outer part of the HFS potential which would otherwise vanish far too quickly at the large r. In fact, all the discussion by MP of the supposed merits of the HFSL potential at large r relate not so much to the *ab initio* aspects of this model but rather to the Latter addition of the hydrogen potential.

III. CONCLUDING REMARKS

We believe that when experimental evidence is available the procedure of testing the accuracy of an atomic potential by comparing results with HF predictions is a dubious one. There are many versions of HF and quoting directly from Kennedy and Manson (KM),[15] "There has been, in the past, no unanimity on what constitutes a Hartree-Fock calculation. There have been two difficulties: First, various possible choices can be made for the potential in which to solve for the final continuum state. Second, the complexity of the HF equation for a continuum orbital is such that numerical errors can crop up fairly easily." KM show that "the results of three different HF calculations for the Ar $3p$-d transition indicate that the various approximations are substantially the same at intermediate distances from the nucleus but much less so at the outer edge of the atom." Yet it is the outer edge of the atom with which most of MP comparisons are concerned, particularly the comparisons involving the photoionization cross section.

The final criteria of the accuracy of any calculation should be how well the result of a calculation agrees with experiment, not how well the result agrees with another theory. The GSZ potential is not intended as a new theory of the atomic potential. It is a simple, phenomenological central potential which can be used to generate wave functions which can be used to calculate atomic properties needed in aeronomy, astrophysics, and the like. For such applications, the potential should yield atomic properties which are in good agreement with experiment. We do not feel that Manson and Purcell have demonstrated that the HFSL potential yields atomic properties which are in better agreement with experiment than those obtained from the GSZ potential. They have demonstrated that the HFSL potential in its description of the atomic potential of the noble gases yields results closer to HF results than does the GSZ potential, but this certainly does not mean the HFSL potential is better approximation of the best average atomic potential than is the GSZ potential.

MP also state that the GSZ potential obtained by fitting valence excitations is relevant only to outer subshells. However, eigenvalue comparisons[4] with experimental energy levels for inner subshells indicate that GSZ potential is also quite good in characterizing inner shells. In addition, MP have ignored works in which the GSZ potential parameters are adjusted by the *ab initio* energy minimization procedure of Bass, Green, and Wood.[16-18] The potential obtained by such a procedure should accurately describe the inner atomic states.

Lastly, let us suggest that perhaps this controversy can be channeled into more constructive channels by discussing what approaches might be taken towards the further development and application of atomic independent particle models. We have already mentioned the extensive developments known as the $X\alpha$ method.[11,13,14] The recent work of Talman and Shadwick,[19] who derive a self-consistent set of equations leading to a numerical atomic central potential which minimizes the total energy, is important in that their effective potential naturally behaves like $-2/r$ for large r.

Another recent development is the comparative study of McGuire[20] which suggests that a Born-approximation cross section, using the IPM of GSZ, tends to give results closer to multi-configuration ground-state calculations rather than to single configuration ground-state calculations. This supports the view in DGG that the "tunable" nature of the GSZ analytic potential permits the incorporation of extra physical input into the model.

Perhaps we can conclude this matter by agreeing that we have reached the point in atomic physics and application of atomic physics where the complexities associated with the nonlocal character of the true potential acting on each atomic electron play a significant physical role. Hence we must commence the process of trying to characterize these nonlocal aspects in manageable ways. In this regard, atomic physics might well look to nuclear physics since in nuclear physics nonlocal effects arise not as fine details but rather as major physical effects arising largely from the short range and complex nature of the basic nuclear force. Many extensive studies have been carried out with nonlocal potentials in nuclear physics[21-24] which could be helpful at the present phase of atomic physics. In many of these studies analytic potentials both local and nonlocal have served a very useful role. Thus much remains to be done not only in borrowing the experiences of nuclear physics for atomic physics, but also in applying in return what is learned thereby to nuclear physics.

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