Photoionization and pseudopotentials

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Transferability of norm-conserving pseudopotentials to low-energy electron-molecule scattering processes has been very successful [Bettega et al., Phys. Rev. A 47, 1111 (1993)]. In this paper we discuss the possibility of using effective potentials in calculations of valence electrons photoionization cross sections. Through atomic targets, we illustrate that pseudopotentials can be optimized to give cross sections in good agreement with all-electron calculations. The present work represents a first step towards more elaborate computer programs for photoionization of molecular targets containing heavy atoms.

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Photoionization is one of the best techniques to study molecular and atomic properties. It is being used extensively, as any quick bibliographical search will reveal. Experimental works are followed or preceded by theoretical calculations, as, for instance, in Refs. [1–6]. Most of the theoretical calculations refer to molecules of atoms with low atomic numbers. The reason is simple to understand: the calculations are usually made in the ab initio framework, not in the density functional (DF), so that the needed number of basis functions becomes a very serious limitation. Unless the density functional theory is completely remade, it cannot exactly account for the photoionization because there one loses the good orbital, spin, and total angular-momentum quantum numbers L, S, and J.

To spare ab initio calculations from the number of basis functions limitation, the usual technique to solve electronic structure and electron-scattering problems is to employ pseudopotentials [7,8]. Pseudopotentials were designed for ground-state atomic energy calculations [9–12] and have been shown to work at very different chemical environments, calculation framework (ab initio or DF) [13], for excited states and scattering. Pseudopotentials have a very long history starting back from the orthogonalized plane-wave method for band-structure calculation. Since the early days, many proposals to define the pseudopotential have appeared in the literature: norm-conserving [9–12,14–17], ultrasoft non norm-conserving [18], separable [19], and some very recent proposals as "hardness-conserving" [20]. The history of pseudopotentials is a history of success: whenever they were used, the results were very good and transferability was proven. One of the problems for which pseudopotentials are not being employed is the calculation of valence electrons photoionization cross sections. In what follows we study the possibility of using potentials in such calculations and we find it is possible to optimize them for that purpose.

Our study of the use of pseudopotentials in photoionization calculations is entirely made within the local-density approximation (LDA) for practical reasons. Pseudopotentials defined within LDA are perfectly transferable to ab initio.

The pseudopotentials we will be using are the norm-conserving type of Ref. [10] because they allow a simple optimization through the cutoff radius [21]. The fact that they are not the "softest," from the point of view of a plane-wave basis [17], does not concern us because the pseudopotentials will be used with Gaussian bases. For this very same reason we are not using popular ultrasoft pseudopotentials [18]. The many possible ways in which Gaussian basis sets can be generated [22] makes the optimization of the pseudopotential with respect to the size of a particular basis set of little utility.

To exemplify our procedures, we calculate photoionization of K, which ionizes from

\[ (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^1 \]

to

\[ (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6 \],

and Ga, which ionizes from

\[ (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^10(4s)^2(4p)^1 \]

to

\[ (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^10(4s)^2 \].

The proper way to calculate cross sections within LDA is through the transition state (half occupancy) [23]. Thus one calculates the one-electron LDA states of configurations

\[ (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^{0.5} \]

for K and

\[ (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^10(4s)^2(4p)^{0.5} \]

for Ga. The cross section (in the atomic units \( h = 1 \), \( e = 1 \), \( m = 1 \)) is given by

\[
\sigma_{(n,l)\rightarrow(k,l')}^{(\text{length})} = \frac{8 \pi \omega N_{(n,l)\rightarrow(k,l')}}{3ck} \left| \int_0^\infty u_{(k,l')}^* (r) r u_{(n,l)}(r) dr \right|^2
\]

for a transition from the outermost atomic electron state \( (n,l) \) to the scattering state \( (k,l') \). Of course, \( l' = l \pm 1 \). The

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normalization factors $N_{(n,l)-(k,l')}$ are $N_{(4s^24p^6)}^{(Ga)} = 1$, $N_{(4s^24p^5)}^{(Ga)} = 1/3$ and $N_{(4s^24p^4)}^{(Ga)} = 2/3$.

Aside from the cross section of Eq. (1), named the “length” cross section, we can also calculate the “velocity” cross section defined in terms of the matrix elements of momentum. The two cross sections are related by the commutators of $r$ and $H$ and should be equal if the same Hamiltonian is used for the bound state $(n,l)$ and the scattering state $(k,l')$. This happens if one uses the all-electron one-particle Hamiltonian for the transition state for both the initial and final states. But the equality is not satisfied if one uses pseudopotentials that depend on $l$, the initial and final states having $l$’s that differ by one unit. With pseudopotentials, the velocity cross section diverges much from the all-electron result, thus we will not use velocity cross sections to optimize the pseudopotentials.

To define the pseudopotential within the framework of Ref. [10] one must ask the following:

(i) What is the exchange-correlation expression. (We use that of Ref. [24] parametrized in Ref. [25].)

(ii) What is the atomic configuration? [Unless otherwise

FIG. 1. Absorption cross section for the outermost Ga valence electron calculated for the transition state. Full circles, the all-electron results; squares, configuration $(\text{core})\,(4s^2)(4p)^{65}$ and optimized cutoff radii $r_c$ (1.37 for $l=1$ and 0.96 for $l=0$), which gives minimum errors compared to all-electron method; open circles, configuration $(\text{core})(4s)^2(4p)^{65}$ but with the cutoff radii of Ref. [15]; open triangles, the ground-state configuration $(\text{core})(4s)^2(4p)^1$, used in Ref. [15], but with our “optimal” cutoff radii.

FIG. 2. Pseudopotential of optimized cutoff and transition state (squares in Fig. 1) compared with the pseudopotential of Ref. [15]. The latter has a different defining configuration and cutoff.

FIG. 3. Absorption cross section for the outermost Ga valence electron calculated for the transition state. The all-electron results are compared with the optimized pseudopotential. As in Fig. 1, the failure happens at higher energies. Observe the large resonance at 0.05 eV caused by the 4$d$ state.

FIG. 4. Absorption cross section for the outermost K valence electron calculated for the transition state. The all-electron results are compared with the optimized pseudopotential for the K core of 18 electrons and the pseudopotential for a reduced core (and increased valence band) of only ten electrons. Observe that the latter pseudopotential corrects the higher-energy failure, but fails at the low energies.
specified, we use the transition state configuration, namely 
(\text{core})(4s)^{0.5}$ for $K$ and $(\text{core})(4s)^{2}(4p)^{0.5}$ for $Ga$.

(iii) What are the cutoff radius $r_c$? (We minimize the error of the pseudopotential absorption cross section with respect to all-electron, by adjusting the cutoff radii.)

(iv) What is the cutoff function? (We use $\exp[-(r/r_c)^{3.5}]$ of Ref. [15].)

In Fig. 1 we show the absorption cross section for the ionization process $Ga_{(4s)^2(4p)^2} \rightarrow (4s)^1$ calculated for all-electron and for different pseudopotentials. The cross sections are calculated with the transition state configuration, though the configurations defining the pseudopotentials do vary. One notices that all pseudopotentials fail at higher energies, when comparing with the all-electron results, though the pseudopotential with optimized cutoffs (squares) perform slightly better. This failure is related to the fact that, at high energies, the photoelectron is scattered by the high linear-momentum $k$ components of the potential in a momentum space picture and those are the components of the potential, which are removed from the pseudopotentials (softness). At lower energies, the results obtained with the pseudopotential defined with the ground-state configuration fails badly (notice that we are using a log scale). The reason for this failure is understandable: at low energies, the cross sections are much dependent on where the higher bound states are placed. These higher bound states (infinite in number in the case of an ion) are responsible for resonances at low energies.

In Fig. 2 we compare our optimized pseudopotential with that of Ref. [15]. They differ mostly in the flat region near the origin. That is only natural, because this flat region is chosen so that the pseudopotential eigenvalue coincides with the all-electron eigenvalue, and the two pseudopotentials, coming from different configurations, have different sets of eigenvalues.

In Fig. 3 we study the $Ga_{(4s)^1(4p)^2}$ transition. Again the optimized pseudopotential goes very well but fails at higher energies. One notices a large resonance at $0.05$ eV.

In Fig. 4 we take the case of the $K_{(4s)^2(4p)^2} \rightarrow (4s)^1$ ionization. Aiming at correcting the high-energy misbehavior, we also considered a $K$ atom with a reduced core. Of course, a reduced core means an expanded valence so that part of the pseudopotential advantage is lost. In the case of the reduced core, the one-electron states $3s$ and $3p$ have zero radial nodes, but the $4s$ state has one node. One sees from the figure that reduced core does indeed improve the high-energy limit, at the expense of a worse behavior at low energies.

To conclude, we may say that it is possible to construct pseudopotentials suitable to photoionization calculations. The pseudopotentials of Ref. [10] allow a choice of an adequate configuration and cutoff optimization. Though these pseudopotentials are not the favorite of modern solid-state calculations, because they are not the “softest” from the plane wave point of view, they are flexible enough to allow very good fits to all-electron results, and are soft enough when used with Gaussian bases.

[21] However, those authors and Ref. [15] did not think the cutoff radius was a parameter to be played with. The FORTRAN code we used, originally made by S. Froymen, enlarged by N. Troullier, and with contributions from many researchers, is sufficiently flexible to allow these studies.