

Oscillator strengths with pseudopotentials

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The accuracy of the time-dependent local-density approximation (TDLDA) for group-IB elements is preserved under the additional approximation of using pseudopotentials to treat the effects of core electrons. This extends the work of Zangwill and Soven, who showed the utility of the all-electron TDLDA in the atomic response problem, and justifies using pseudopotentials in calculating the far-ultraviolet response of multiatom systems. [S1050-2947(98)00709-4]

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I. INTRODUCTION

Mean-field theory is now widely used in chemistry and condensed-matter physics, treating the electron-electron interaction in the local-density approximation [1]. An additional approximation that is often made in multiatom calculations is to use pseudopotentials for the ionic part of the Hamiltonian [2] to avoid explicit calculation of the core electrons. The static theory is remarkably successful in describing binding and ground-state properties. The dynamic theory based on these Hamiltonian approximations, the time-dependent local-density approximation (TDLDA), is also quite tractable numerically and often gives an excellent description of the strong transitions [3–9].

In simple systems such as atoms, TDLDA computations are quite feasible without making the pseudopotential approximation [10–13] or even the local-density approximation.¹ However, for many-atom systems with three-dimensional bases such as plane-wave or coordinate-space meshes, the use of pseudopotentials is practically unavoidable. This is the general motivation of this study comparing the pseudopotential approximation to the all-electron calculation of the atomic response. The quality of the TDLDA approximation depends of course on the excitation energy and on the detail one requires. At low energies, in the region of the discrete transitions, the TDLDA provides overall account of the oscillator strength as a function of excitation, but the details of transition energies and strengths are given much more accurately by more sophisticated techniques. At energies above the ionization threshold, the experimental spectra do not have so much detail and the TDLDA is arguably the most effective approximation available. As one goes up in energy, the dynamic electron-electron interaction decreases in importance, and the TDLDA becomes an unnecessary refinement on the

independent-electron Hartree-Fock approximation. Of course about the thresholds for core excitation, the pseudopotential TDLDA is invalid, since it does not treat core degrees of freedom explicitly.

II. OSCILLATOR STRENGTHS IN IB ATOMS

The question of the validity of the pseudopotential approximation in the lower energy domain arose in our studies when we tried to apply TDLDA to clusters made from group-IB elements, i.e., Cu, Ag, and Au. In these elements, the closed d shell just below the valence s shell is important to the dynamics and cannot be treated in a frozen approximation. However, we found when we calculated the TDLDA response of small Ag clusters including the d -shell electrons that the f -sum rule for the valence electrons was badly violated. Since the f -sum rule counts the number of electrons, we expected the sum rule to equal the number of valence electrons in the pseudopotential calculation. In fact, this is not the case because the pseudopotential is nonlocal. The pseudopotentials necessarily depend on the angular momentum l of the electron (with respect to the ion), and the double commutator that gives the sum rule for a closed l shell has a contribution from the potential given by

$$\Delta f_l = \frac{2l+1}{3} \frac{2m}{\hbar^2} \int r^4 dr |\phi_l(r)|^2 \times \left(-V_l(r) + \sum_{\pm} (l \ 0 \ 1 \ 0 | l \pm 1 \ 0)^2 V_{l \pm 1}(r) \right), \quad (1)$$

TABLE I. Oscillator strengths f for pseudopotential calculations of IB atoms

Element	Kinetic	With pseudopotential	TDLDA $I(400)$
Cu	11	24.9	20.9
Ag	11	19.5	18.8
Au	11	21.9	21.3

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¹The atomic response with exact exchange, called time-dependent Hartree-Fock or RPAE, is discussed in Ref. [14].

TABLE II. Energies and strengths of the $s \rightarrow p$ transition in IB metal atoms

		Free	TDLDA all-electron	TDLDA pseudo- potential	Many- body [24,28]	Expt. [25,26,29]
Cu	E (eV)	3.9	4.1	4.2	3.9	3.8
	f	0.82	0.42	0.32		0.66
Ag	E (eV)	3.9	4.1	4.1		3.7
	f	0.89	0.51	0.50		0.7
Au	E (eV)	5.1	5.2	5.3	5.3	4.9
	f	0.98	0.30	0.35	0.6	0.5

where $\phi_l(r)$ is the radial wave function of the electron and $V_l(r)$ is the pseudopotential for angular momentum l . In the IB atoms with explicit treatment of outer s and d electrons, the ordinary sum rule arising from the kinetic energy operator gives $f=11$, the number of active electrons. The potential roughly doubles this, which may be seen from the numbers in Table I. The second column gives the total oscillator strength with only the kinetic part of the Hamiltonian, and the third column gives the result including the pseudopotential contribution from Eq. (1) as well. The qualitative effect of a nonlocal pseudopotential on oscillator strengths in clusters of the group-IA atom lithium has been recently discussed in Ref. [15]. Here the nonlocality induces an effective mass to lower the oscillator strength of the collective valence transition.

There are several possibilities to interpret the large oscillator strength in the pseudopotential of IB atoms. The best outcome for theory would be if the pseudopotential TDLDA were still accurate in the low-energy domain, and the extra f strength is physical and due to indirect effects of the core electrons. Another possibility is that the extra strength is an artifact of the nonlocality of the pseudopotentials. In that case we ask further whether the approximation introduces spurious strength in the spectroscopic domain or only in the higher energy domain, where it would be less significant to present applications of the TDLDA.

We shall study the atomic response of group-IB elements following closely the method of Zangwill and Soven [10]. The independent-electron response, given by

$$\Pi^0(\vec{r}, \vec{r}', \omega) = \sum_{i,j} \phi_i^*(\vec{r}) \phi_i(\vec{r}') \phi_j^*(\vec{r}') \phi_j(\vec{r}) \times \frac{2(e_i - e_j)}{(e_i - e_j)^2 - \omega^2 - i\eta}, \quad (2)$$

is represented on a radial coordinate space mesh with an angular momentum decomposition. The sum over particle states in Eq. (2) is replaced by the single-particle Green's function, greatly simplifying the treatment of the continuum.² The interacting response is then computed by the matrix equation

²This technique was first applied to calculate nuclear response functions [16].

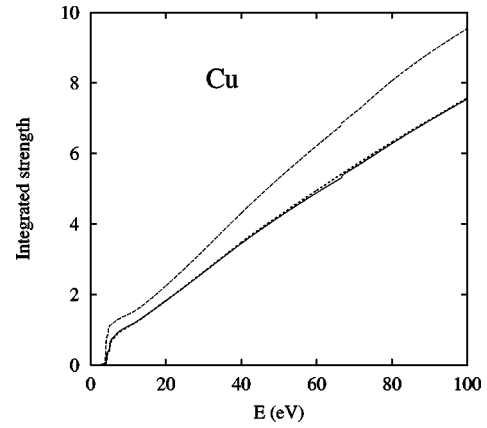


FIG. 1. Integrated transition strength in Cu: all-electron TDLDA (solid line); pseudopotential TDLDA (short dashed line); static LDA (long dashed line).

$$\Pi^{\text{TDLDA}} = \Pi^0 (1 - v \Pi^0)^{-1}, \quad (3)$$

where v is the electron-electron interaction. The interaction v includes the local-density approximation to the exchange and correlation energy given by the parametrization of Ceperley and Alder [17,18]. The relativistic treatment of the Hamiltonian and Green's function is necessary to get reasonable agreement with spectroscopic properties for the Ag and Au calculations. The construction of a relativistic Green's function is discussed in Refs. [19,20].

Our pseudopotentials are calculated by the procedure of Troullier and Martins [21]. There is a single parameter in constructing the pseudopotential, the radius a at which the potential joins the all-electron self-consistent potential, which is used for the outer regions. In principle, the physical quantities should be insensitive to the choice of a , provided it is well outside the nodal radii of the valence wave function. In this study we have used values $a = 1.1 \text{ \AA}$ for s , d , and f orbitals in Cu and Ag, and $a = 1.21 \text{ \AA}$ for the p orbitals. In Au, we took $a = 1.24 \text{ \AA}$ for all orbitals. As a consistency check, we show in Table I the integrated TDLDA response calculated up to 400 eV. The integrated response $I(\omega)$ is given by the following integral over $\text{Im } \Pi$:

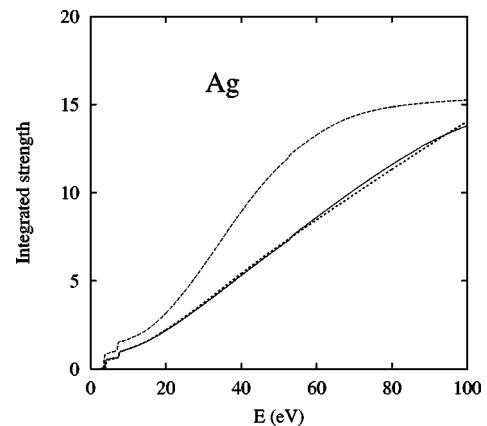


FIG. 2. Integrated transition strength in Ag: all-electron TDLDA (solid line); pseudopotential TDLDA (short dashed line); static LDA (long dashed line).

$$\begin{aligned}
 I(\omega) &= \int_0^\omega d\omega' \frac{df}{d\omega} \\
 &= \frac{2m}{\pi\hbar^2} \int_0^\omega d\omega' \int dr dr' z z' \text{Im} \Pi^{\text{TDLDA}}(r, r', \omega').
 \end{aligned}
 \tag{4}$$

It may be seen from Table I that TDLDA conserves the sum rule and the integrated strength agrees with the double commutator, as it must.

We now compare the pseudopotential response with the all-electron response in the different energy domains, first examining the spectroscopic transitions. The strong $s \rightarrow p$ excitation is calculated in various approximations with the results shown in Table II. In the case of Au, the energies and transition strengths are the weighted averages for the $s_{1/2} \rightarrow p_{1/2}$ and $s_{1/2} \rightarrow p_{3/2}$ excitations. The independent-particle LDA is computed from the Π^0 response and is shown in the first column. The transition in the TDLDA, shown in the next column, has nearly the same energy but a quenched strength due to screening by the d -shell electrons. The screening effect amounts to a 40–60 % reduction of the transition strengths. This illustrates the advantage of the TDLDA, that it incorporates the screening automatically, unlike some other treatments [22,23]. The pseudopotential approximation gives very similar energies and transition strengths, as shown in the third column. For completeness we also compare with experiment, although the well-known deficiencies of the LDA make this an unreliable application. The empirical strengths show a screening somewhere between the TDLDA prediction and the independent-particle value.

We next turn to the continuum domain. Figures 1–3 shows the integrated response for the IB atoms for the energy domain 0–100 eV. The steep rise in I below 10 eV is due to the pair of discrete transitions $s, d \rightarrow p$ given in Table II. One can also see a small feature around 50–70 eV due to the transition from a deeply p state to the partially occupied valence s state. This transition is absent in the pseudopotential calculation. Note that the TDLDA strength is quenched with respect to the independent-particle response by about 10–20% even up to the higher energies. Comparing the pseudopotential and all-electron calculations, we see that they are practically indistinguishable in the case of Cu and Ag. They also track well in Au below 80 eV. Above 80 eV, the pseudopotential approximation deviates significantly from the all-electron calculation in Au. This might be a relativistic effect: the all-electron calculation must be done rela-

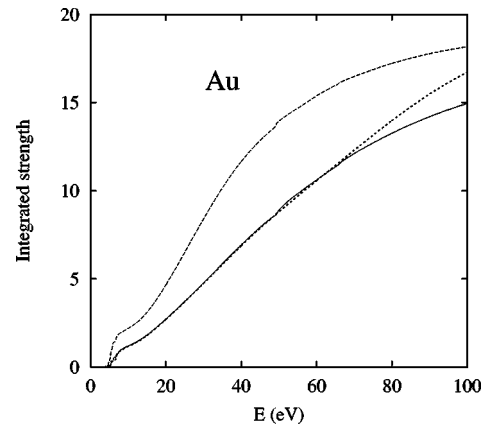


FIG. 3. Integrated transition strength in Au: relativistic all-electron TDLDA (solid line); pseudopotential TDLDA (short dashed line); relativistic static LDA (long dashed line).

tivistic in Au, but the pseudopotential is treated nonrelativistically. Concerning the empirical strength function in the continuum region, we have not found any experimental data for isolated atoms. The absorption of thin films has been well-studied [27], and the deduced atomic absorption, naively neglecting the interaction of the atoms, is closer to the independent electron response than to the TDLDA predictions. However, the interaction between atoms is certainly not negligible below 100 eV, and one should compare with a TDLDA calculation of the metal.

III. CONCLUSION

We have found that the TDLDA with a pseudopotential approximation gives virtually the same distribution of oscillator strength in the region 0 – 100 eV as the all-electron theory of IB atoms, despite the fact that the f -sum rule is badly violated by the state-dependent interaction. We conclude that the pseudopotentials in these atoms properly take into account many-body effects by the nonlocality of the potential, and may be used with confidence in studying the response of these elements.

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