ROLE OF SELF-INTERACTION CORRECTIONS IN THE PHOTOABSORPTION CROSS SECTION OF SMALL METAL CLUSTERS

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ABSTRACT. The Time Dependent Local Density Approximation (TDLDA) is modified to incorporate the Self-Interaction Correction (SIC) of Perdew and Zunger. It is then applied to study the static polarizabilities and phoabsorption cross sections of small, spherical, neutral metal particles with 8, 20, and 40 Sodium atoms.

1. Introduction

The LDA of Density Functional Theory (DFT) and its extension[1] - TDLDA - to describe excited states of many-electron systems are self-interacting approximations. The success of the Self-Interaction Correction[2] (SIC) in describing the Ground State (GS) properties of diverse many-electron systems[3], prompts for the study of its implications in the determination of their excitation spectra. We shall tackle this question within the field of metal clusters, by calculating their photoresponse.

The SIC leads to a departure from mean-field theory, so that the general TDLDA formalism developed in ref.[1] is no longer applicable. Therefore, in this paper we reformulate TDLDA to make it suitable for inclusion of SIC (we shall henceforth denote this formalism as SIC-TDLDA). The paper is organized as follows. In section 2 we summarize the SIC corrections and discuss its implications in the ground-state properties of metal clusters; section 3 is devoted to the study of their photoabsorption spectrum and conclusions are collected in section 4.

2. Gound state properties

In the jellium model, the SIC-LDA single-particle potentials read[2]

$$V^{(i)}_{SIC}(\vec{r}) = V_I(\vec{r}) + e^2 \int \frac{[n(\vec{r}\,') - n_i(\vec{r}\,')]d\vec{r}\,'}{|\vec{r} - \vec{r}\,'|} + V_{xc}[n(\vec{r})] - V_{xc}[n_i(\vec{r})] \qquad (1)$$

where $n(\vec{r}) = \sum_{i=1}^{N} |\psi_i^{(i)}(\vec{r})|^2$, $n_i(\vec{r}) = |\psi_i^{(i)}(\vec{r})|^2$, N denotes the total number of valence electrons in the cluster, and $V_I(\vec{r})$ the jellium potential of N positive ions (Wigner-Seitz radius $r_s = 4\ a_0$). For V_{xc} we take the parametrization of ref.[4]. We

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denote by $\psi_j^{(i)}(\vec{r})$ the eigenfunction and by $\epsilon_j^{(i)}$ the associated eigenvalue with quantum numbers j, solutions of the "Kohn-Sham"-like equation for potential $V_{SIC}^{(i)}(\vec{r})$,

$$\left[\frac{-\hbar^2}{2m} \Delta + V_{SIC}^{(i)}(\vec{r}) \right] \psi_j^{(i)}(\vec{r}) = \epsilon_j^{(i)} \psi_j^{(i)}(\vec{r}) \,. \tag{2}$$

The results for the self-consistent solution of equations (1),(2) are shown in fig.1 for Na_{20}, in comparison with standard LDA results.

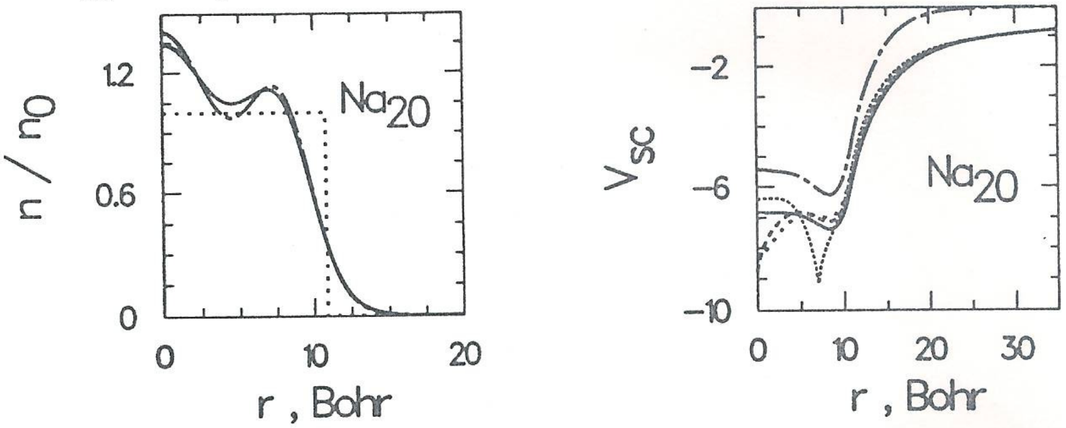

FIG 1. LEFT: The LDA radial density (in units of the jellium density n_0) is drawn with a bar dashed line, whereas the SIC-LDA density corresponds to the full drawn curve. **RIGHT:** The LDA mean field potential is drawn with a bar-dashed line; The other four curves correspond to the "1s", "1p", "1d" and "2s" orbital SIC-LDA potentials, drawn with full curve, thick dashed curve, dotted curve and thin dotted curve.

Although hardly discernible, the SIC-LDA density extends effectively more outside of the jellium edge, as can be inferred from the results of table 1 for the static polarizabilities.

N	$TDLDA$	$SIC-TDLDA$	EXP
8	1.41	1.52	1.72 ± 0.03
20	1.34	1.46	1.58 ± 0.04
40	1.30	1.41	1.56 ± 0.03

table 1. Static polarizabilities of Na_8 Na_{20} and Na_{40}, in units of $R_0^3 = Nr_s^3$ as calculated with TDLDA and SIC-TDLDA. EXP stands for the experimental values taken from ref.[5].

In the right panel, the four different potentials corresponding to the four orbital quantum numbers of occupied states in Na_{20} are significantly deeper than the single mean-field LDA potential and display a common, physically correct Coulomb tail, into which all merge somewhere outside of the jellium radius, in contrast with the tail of the LDA potential, determined essentially by V_{xc} in eq.(1).

3. Photoabsorption cross section

The standard expression for the LDA independent particle susceptibility reads[1]

$$\chi_0(\vec{r},\vec{r}\,';\hbar\omega)=\sum_i^{occ}\psi_i^*(\vec{r})\psi_i(\vec{r})[G(\vec{r},\vec{r}\,',\epsilon_i+\hbar\omega)+G^*(\vec{r},\vec{r}\,',\epsilon_i-\hbar\omega)]\ . \tag{3}$$

The sum extends over all occupied single particle states. The Green's functions include all (infinite) electronic transitions from each of the occupied single particle states, and the 2 terms in square brackets ensure the exact cancellation of the transitions which explicitly violate the Pauli principle. In SIC-LDA, however, from each of the occupied single particle states, to which corresponds a specific single particle potential, there is an infinite number of possible electronic transitions, which should promote the electron into a state which is also SIC corrected. The natural choice is therefore to compute the orbitals into which the electron is to be promoted with the potential appropriate for the initial state of the electron[2, 6]. This, in turn, amounts to define orbital dependent Green's functions, in a straightforward correspondence with the originating orbital dependent potential. However, care must be exercised, so that the Pauli principle is not violated, which amounts to subtract explicitly the finite number of violating terms. This leads to,

$$\begin{aligned}\chi_0(\vec{r},\vec{r}\,';\hbar\omega)=&\sum_i^{occ}\psi_i^{(i)^*}(\vec{r})\psi_i^{(i)}(\vec{r}\,')\left[G^{(i)}(\vec{r},\vec{r}\,',\epsilon_i^{(i)}+\hbar\omega)-\sum_j^{occ}\frac{\psi_j^{(i)}(\vec{r})\psi_j^{(i)^*}(\vec{r}\,')}{\epsilon_i^{(i)}+\hbar\omega-\epsilon_j^{(i)}+i\delta}\right]\\ +&\sum_i^{occ}\psi_i^{(i)}(\vec{r})\psi_i^{(i)^*}(\vec{r}\,')\left[G^{(i)^*}(\vec{r},\vec{r}\,',\epsilon_i^{(i)}-\hbar\omega)-\sum_j^{occ}\frac{\psi_j^{(i)^*}(\vec{r})\psi_j^{(i)}(\vec{r}\,')}{\epsilon_i^{(i)}-\hbar\omega-\epsilon_j^{(i)}-i\delta}\right],\end{aligned} \tag{4}$$

the sums being restricted to the set of single-particle quantum numbers corresponding to occupied orbitals in the GS.

Once $\chi_0(\vec{r},\vec{r}\,';\hbar\omega)$ is determined the SIC-TDLDA susceptibility is now calculated as the solution of the following integral equation[7]:

$$\chi(\vec{r},\vec{r}\,';\hbar\omega)=\chi_0(\vec{r},\vec{r}\,';\hbar\omega)+\int d\vec{r}\,''d\vec{r}\,'''\chi_0(\vec{r},\vec{r}\,'';\hbar\omega)K(\vec{r}\,'',\vec{r}\,''')\chi(\vec{r}\,''',\vec{r}\,';\hbar\omega)\ , \tag{5}$$

where the screening kernel reads (we do not perform SIC in $K(\vec{r},\vec{r}\,')$),

$$K(\vec{r},\vec{r}\,')=\frac{e^2}{|\vec{r}-\vec{r}\,'|}+\frac{dV_{xc}}{dn}\delta(\vec{r}-\vec{r}\,')\ . \tag{6}$$

Due to the spherical symmetry of the clusters we consider here, the dipole polarizability can then be written(for details, cf. ref.[7]),

$$\alpha(\hbar\omega) = -e^2 \frac{4\pi}{3} \int_0^{+\infty} dr\, r^3 \int_0^{+\infty} dr'\, r'^3 \chi_{L=1}(r, r', \hbar\omega)\ . \tag{7}$$

Finally, the photoabsorption cross section $\sigma(\hbar\omega)$ is simply related to the imaginary part of the polarizability by $\sigma(\hbar\omega) = (4\pi\omega/c)Im[\alpha(\hbar\omega)]$.

The calculated values for the static polarizabilities of Na_8, Na_{20} and Na_{40} are collected in table 1, together with the experimental values taken from ref.[5] and the TDLDA results. The SIC-TDLDA provides a systematic improvement with respect to TDLDA[8], towards the experimental values.

In fig.2 the results of the SIC-TDLDA dynamical response are depicted with solid lines; dashed lines show the previously calculated TDLDA results[7]. The SIC-TDLDA response is systematically red-shifted with respect to the TDLDA, in direct relation with the change in the static polarizabilities. Furthermore, the pattern of Landau fragmentation is not significantly changed from TDLDA to SIC-TDLDA, apart from the general trend of SIC-TDLDA to spread the collective response over a wider energy interval. In particular, one observes the systematic appearance of small humps in the ultraviolet(UV) part of the spectra, a feature which is directly related to the (now) physically correct Coulomb tail of the SIC-LDA potentials.

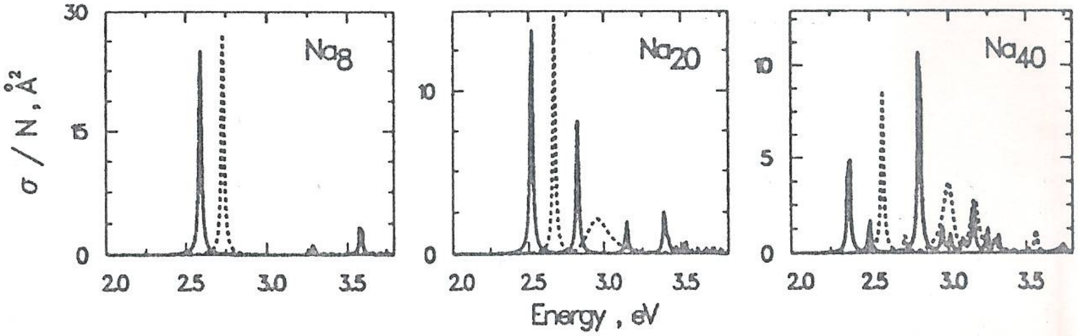

FIG 2. Photoabsorption cross sections per atom for Na_8, Na_{20}, and Na_{40}, in $\mathring{A}^2$, calculated making use of the SIC-TDLDA (full lines) and TDLDA(dashed lines). In all cases the value used for the infinitesimal delta (cf. eq.(4) and ref.[7]) was 10 meV.

In sharp contrast with the LDA case, the SIC-LDA potentials accomodate an infinite number of bound states. However, and because their overall depth (see fig.1) is significantly lowered, the wave-functions of the occupied states are very similar. Remaining well localized, the occupied states will not overlap significantly with the loosely bound Rydberg states, preserving the essential featues of the Landau fragmentation pattern. Note finally, that since the SIC-TDLDA conserves the Thomas-Reiche-Kuhn (TRK) sum rule the occurrence of the UV humps implies a reduction of total strength in the visible region.

Comparison with experiment is carried out in fig.3 for Na_8, for which there is the most detailed experimental information. To this end, the damping mechanisms discussed in ref.[9] and not present in SIC-TDLDA were simulated by folding the results of fig.2 with normalized Lorentzian functions, including the appropriate damping ratio ($\Gamma/\hbar\omega = 0.1$, in accord with the findings in ref.ref.[9]).

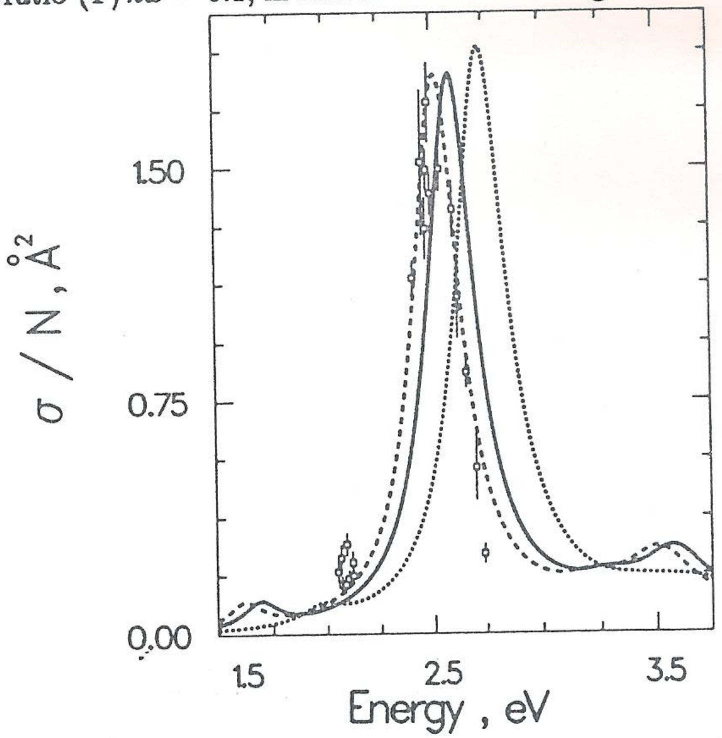

FIG 3. Experimental values for the photoabsorption cross section per atom for Na_8, in $\AA^2$, taken from ref.[10] are drawn with small squares. The results of the present SIC-TDLDA calculation correspond to the full drawn curve. The dashed curve corresponds to red-shifting the SIC-TDLDA results by 3% so as to bring the calculated plasmon peak to its most probable position. Finally, the thin dotted curve represents the TDLDA result for Na_8.

The SIC-TDLDA results (full line) display a better agreement with experiment than TDLDA (dotted line). They are, however, $\approx$ 3% blue-shifted with respect to the experimental peaks. For comparing the folded SIC-TDLDA lineshapes with the experimental results, we purposely shifted the dynamical response by 3%, the resulting curve being displayed with a dashed line. While the overall features of the data seem to emerge from the present formalism, we note that the SIC-TDLDA predicts a sizeable acummulation of strength in a region of the absorption spectrum not yet measured. It would be interesting to resolve this part of the spectrum experimentally, in order to confirm whether or not the sum rule strength which seems to be missing in present-day experimental results, is indeed to be found in the UV region of the spectrum, as predicted by the SIC-TDLDA.

4. Conclusion

The TDLDA has been modified to incorporate SIC corrections. It was applied specifically to neutral metal clusters, and comparison with experimental data favours this model with respect to the TDLDA. The SIC-TDLDA provides a simple framework which requires little extra computational effort, being able to overcome many of the unpleasant features intrinsic to the LDA. Furthermore, this new framework opens the possibility of studying the excitation spectra of negatively charged many-electron systems, to which LDA is often not even applicable. Work along these lines will be published elsewhere.

References

[1] A. Zangwill, P. Soven, Phys. Rev. **B21** (1980) 1561;

[2] J. P. Perdew, A. Zunger, Phys. Rev. **B23** (1981) 5048;

[3] J. P. Perdew, in "Local density approximations in Quantum Chemistry and Solid State Physics", J. P. Dahl and J. Avery Edts.,(Plenum 1982), pag. 173;

[4] O. Gunnarsson, B. I. Lundqvist, Phys. Rev. **B13** (1976) 4274;

[5] W. D. Knight et al., Phys. Rev. **B31** (1985) 2539;

[6] W. J. Hunt, W. A. Goddard, Chem. Phys. Lett. **3** (1969) 414;

[7] W. Ekardt, Phys. Rev. Lett. **52** (1984) 1925; Phys. Rev. **B31** (1985) 6360;

[8] Results for static polarizabilities, making use of the modified Sternheimer equation and using a different SIC model have been reported before in P.Stampfli and K. H. Benemann, Phys. Rev. **B39** (1989) 1007;

[9] J. M. Pacheco, R. A. Broglia, Phys. Rev. Lett. **62** (1989) 1400.

[10] K. Selby et al., Phys. Rev. **B43** (1991) 4565;