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Plasmons and excitons in many-electron systems and the optical response of atomic clusters

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Abstract. In this paper we investigate the sensitivity of the optical response of small atomic clusters of simple metals to the underlying approximations utilized in the calculation of their quasi-particle properties. In spite of the appreciable quasi-particle gaps induced by quantum size effects, it is found that the repulsive part of the irreducible particle-hole interation dominates at all excitation energies, inhibiting the formation of excitonic states. This result is obtained independently of the quasi-particle picture utilized. However, this picture plays an important role in determining the resulting optical absorption profiles. Comparison with experimental data shows that simpler and traditional time dependent local density approximation calculations provide an accurate description of the photoabsorption phenomena in metallic clusters.

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Atomic clusters provide an ideal tool to study the electronic properties of many-electron systems, as their size evolves from that of the simplest molecule – a dimer – to the bulk form of the same material. Among the countless combinations and types of clusters one is able to form nowadays, clusters made out of atoms of simple metals have played a prominent role, mostly due to the fact that it was in the process of their study that shell structure was put in evidence.

The scattering of light by metal clusters constitutes an old field of research, and caught the attention of eminent scientists such as Rayleigh, Mie and others. However, only in the mid-eighties the seminal work of Ekardt [1] has put in evidence the microscopic nature of the photoabsorption and photoemission phenomena taking place in small metallic particles. The underlying microscopic model utilized by Ekardt was the Time-Dependent Local Density Approximation (TDLDA), intuitively introduced by Zangwill and Soven in 1980 [2]. TDLDA, though lacking a first-principles justification, has turned out to be working extremely well in the description of many-body effects in atoms [2], molecules [3], clusters [1], and solids [4]. A common feature of all these examples is the charge density character of these collective states. However, and besides this type of correlated particle-hole motion there is another one well known from the optical properties of semiconductors, ionic solids, and rare gases as well, namely, the bound states of particles and holes, which generally occur if the attractive part of the general particle-hole irreducible interaction [5] dominates. Whereas in metals this does not happen, because the screened particle-hole interaction does not support bound states for usual values of the Thomas-Fermi screening vector [6], the occurrence of such bound states in small metal particles cannot be ruled out, because all states are size-quantized [7], meaning that the effective particle-hole interaction is anywhere between a semiconductor ($e^2/\epsilon r$, with ϵ the static dielectric constant) and a metal ($e^2 exp(kr)/r$, with k the Thomas-Fermi screening vector). In TDLDA, the description of such processes is not explicitly included, and therefore it is highly desirable to investigate the occurrence of bound states in a more general framework. This program has been carried out in [8], in which, starting from the work of Sham and Rice [9], we developed a unified description of excitonic and plasmonic excitations which can be cast in a matrix equation which is formally similar to the well-known RPAE equations in atomic physics, with the essential difference of a better description of exchange, which becomes now properly screened. For this reason, we decided to call this formulation as RPA-SE. The RPA-SE equations result from solving the Bethe-Salpeter equation for the two-particle Green's function in the ladder approximation, which corresponds to write for I, the irreducible particle-hole interaction,

$$I(\mathbf{r_1},\mathbf{r_2},\mathbf{r_3},\mathbf{r_4}) = V_{bare}(\mathbf{r_1}-\mathbf{r_2})\delta(\mathbf{r_2}-\mathbf{r_3})\delta(\mathbf{r_1}-\mathbf{r_4}) - \\ - W(\mathbf{r_1},\mathbf{r_2})\delta(\mathbf{r_1}-\mathbf{r_3})\delta(\mathbf{r_2}-\mathbf{r_4}), \quad (1)$$

where V_{bare} is the bare interaction and W is the screened interaction [10]. In this way we can write for the matrix equation, the solutions of which provide the energies and wave-functions of the excitations of the system,

$$\begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = E \begin{pmatrix} X \\ Y \end{pmatrix} \quad (2)$$

where the matrices A and B are defined as

$$A_{ph,p'h'} = (e_p - e_h)\delta_{p,p'}\delta_{h,h'} + < ph'|I|p'h > , \quad (3)$$

$$B_{ph,p'h'} = < pp'|I|h'h > \ . \quad (4)$$

In Eqs. (3),(4), $e_p(e_h)$, are quasi-particle (quasi-hole) energies, whereas the matrix-elements between quasi-particle

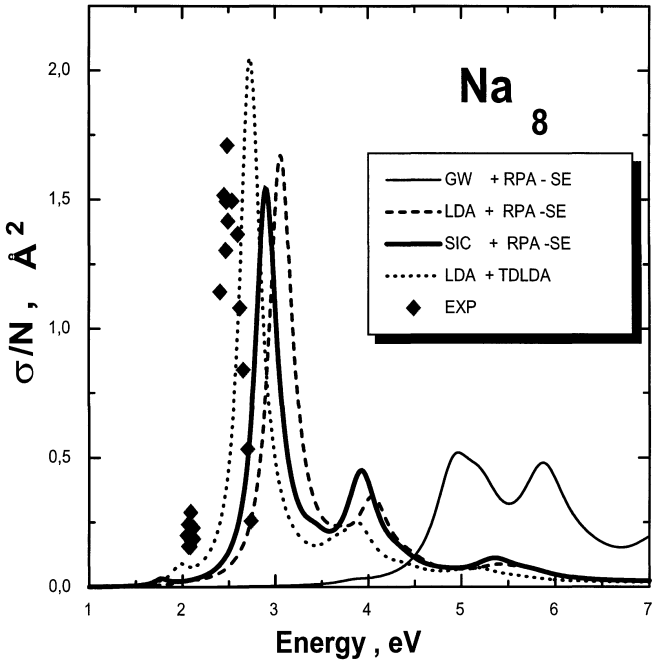

Fig. 1. Photoabsorption cross section per delocalized electron for jellium Na_8 in TDLDA, RPA-SE (see main text for details) utilizing three different approximation for the description of quasi-particle states, and experiment, carried out in clusters at room temperature [14]. The TDLDA curve is shown with a dotted line, the experiment with diamonds, and the RPA-SE results are displayed with three different line types, corresponding to the three different approximations used in the quasi-particle description: LDA (dashed line), SIC (thick solid line) and GW (thin solid line)

states read

$$< ph|\ I\ |p'h' >= \int d\mathbf{r_1}\phi_p{}^*(\mathbf{r_1}) \int d\mathbf{r_2}\phi_h^*(\mathbf{r_2}) \times$$
$$\int d\mathbf{r_3}\phi_{p'}(\mathbf{r_3}) \int d\mathbf{r_4} I(\mathbf{r_1},\mathbf{r_2},\mathbf{r_3},\mathbf{r_4})\phi_{h'}(\mathbf{r_4}) \qquad (5)$$

As becomes clear in the above equations, a quasi-particle description of the electronic states in the system is required, in order to carry out the response calculations. In ref. [8] we took as quasi-particle states the one-electron states obtained by solving the Kohn-Sham equations in the Local Density Approximation (LDA) to Density Functional Theory (DFT). Such an approximation, while crude in principle, leads to the results displayed with a dashed line in Fig. 1, where the lineshape of the photoabsorption cross section of Na_8 is displayed, at different levels of approximation, and compared with experiment, which is represented with diamonds. When a comparison is carried out, on one side with the curve obtained in the more traditional TDLDA (dottedd curve), and on the other side with the experimental data, the results of the RPA-SE deviate more from the experimental data than TDLDA. Taking into account that RPA-SE constitutes, a priori, a superior method for calculating the optical response, it is tempting to assume that its somewhat poorer performance is due to the crude quasi-particle description underlying the RPA-SE results.

In order to check the previous argument in connection with RPA-SE, we start from three independent quasi-particle pictures: The one used in the original work (LDA), an improved description of quasi-particle states in clusters known as Self-Interaction Corrected LDA (SIC) [12], and finally, the one obtained by computing the quasi-particle states in the GW approximation, following the prescription of Hybertsen and Louie [11], a framework which is also utilized in the computation of the screened Coulomb interaction W.

The results are shown in Fig. 1, where the thick solid line provides the results for the SIC-LDA approximation, and the thin solid line shows the results of the GW approximation. Figure 1 corresponds to the calculation of the photoabsorption cross section σ per delocalized electron of Na_8, for simplicity treated here in the spherical jellium background approximation [1], which is known to provide an adequate description of magic clusters of simple metals at room temperature. We have performed similar calculations for other magic clusters (20,40,...) and the results obtained display a similar trend, aside from a more pronounced fragmentation of the optical strength.

Direct comparison with experiment clearly favours the SIC approximation for the quasi-particle states. This conclusion, which also applies to larger clusters, correlates well with the role played by other effects not included in the present calculation. Indeed, ionic structure effects, properly incorporating the cluster vibrational temperature, will lead to an overall red-shift of the photoabsorption lineshape. Therefore, it is rewarding that all results obtained in this work lead to a peak in the lineshape which is blueshifted with respect to the experimental data. On the other hand, SIC lacks a first-principles justification, as opposed to the GW approximation, which can be cast in the framework of a many-body perturbation expansion. However, the true GW, originally proposed by Hedin in 1965 [13], requires the self-consistent solution of a system of coupled integro-differential equations, leading to complex quasi-particle energies and wavefunctions. In the Hybertsen-Louie prescription [11], no self-consistency is required, and a perturbed calculation of the quasi-particle energies is carried out instead. Furthermore, not only the quasi-particle energies are real, but also the wavefunctions are taken to be those of the LDA. In this sense, we cannot make definite statements about the GW calculations, being presently engaged in developing a self-consistent GW approximation, in order to further test the theory. Finally, it is noteworthy that irrespective of the quasi-particle approximation used, no indications can be found of any sizeable effects due to the attractive component of the irreducile particle-hole interaction. Indeed, in all cases the repulsive part clearly dominates, and one can observe the emergence of a well defined peak, which can be shown to correspond to a charge density wave of a marked collective nature. Therefore, and at least in what concerns small atomic clusters of simple metals, excitons seem to be absent, and TDLDA confirms itself as an accurate theory to describe the microscopic features of the optical response of such systems.

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