Effective particle-hole interaction and the optical response of simple-metal clusters

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Following Sham and Rice [L. J. Sham and T. M. Rice, Phys. Rev. 144, 708 (1966)], the correlated motion of particle-hole pairs is studied, starting from the general two-particle Green’s function. In this way, we derive a matrix equation for eigenvalues and wave functions, respectively, of the general type of collective excitation of an N-particle system. The interplay between excitons and plasmons is fully described by this set of equations. As a by-product we obtain—at least a posteriori—a justification for the use of the time-dependent local-density approximation for simple-metal clusters.

I. INTRODUCTION

Though there is no exact theorem sanctioning the use of time-dependent density functionals, the time-dependent local-density approximation (TDLDA) as intuitively introduced by Zangwill and Soven in 1980 (Ref. 1) turned out to be working extremely well in the description of many-body effects in atoms,1 molecules,2 clusters,3 and solids.4 A common feature of all these examples is the charge-density character of these collective states. But 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 interaction5 dominates. 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 In small metal particles, the situation is more subtle, because all states are size quantized:7 this implies that the effective particle-hole interaction is anywhere between a semiconductor (e/εr, with ε the static dielectric constant) and a metal (e/exp(kr)/r, with k the Thomas-Fermi screening vector). For this reason, a more general theory is mandatory for the study of the optical absorption by collective states in metal clusters. Recalling the general discussion on the interplay between excitons and plasmons in the past,8,9 the study of the general two-particle green’s function seems to constitute a promising tool to answer the question of whether or not the oversimplifying of the TDLDA has to be replaced by a more complete theory, in order to obtain a satisfactory insight in the complete nature of collective states in metal clusters. Starting from the method of Sham and Rice,10 an effective equation is derived in Sec. II, for the calculation of the optical spectra in metal clusters. Using the well-established jellium model,1 these equations are solved for a number of Na-jellium clusters in Sec. III. Finally, the conclusions and the comparison with alternative models of calculating the optical response in metal clusters are presented in Sec. IV.

II. THEORY

We are interested in investigating the properties of excitons and plasmons in general many-electron systems. Therefore, our starting point is the full two-particle Green’s function, suitable to describe excitations of such a system involving the correlated motion of two quasiparticles. It will be shown that a unified description of excitonic and plasmonic excitations leads to a matrix equation, which is formally similar to the well-known random-phase-approximation exchange (RPAE) equations in atomic physics, with the essential difference of a better description of exchange, which becomes now properly screened. This formal similarity is, of course, not accidental, and reflects the many possible ways one can derive the equations of motion for these excitations.

Following Sham and Rice10 we start by defining, field theoretically, the exciton/plasmon wave function,

\[ f_\lambda (r_1, r_2, \omega) = \langle N, 0 | \psi^\dagger (r_2), \psi (r_1) | N, \lambda \rangle \]

\[ = \lim_{\eta \to 0} \frac{1}{2\pi i} \int d\omega_1 e^{i\omega_1 \eta} G_{0,\lambda} (r_1, \omega_1; r_2, \omega - \omega_1) , \]

(1)

in terms of the appropriate function \( G_{0,\lambda} \), which occurs in the Fourier transform of the general two-particle Green’s function and is defined as follows:10

\[ G_{0,\lambda} (r_1, \omega_1; r_2, \omega_2) = \sum_\alpha \langle N, 0 | \psi (r_1) | N + 1, \alpha \rangle \langle N + 1, \alpha | \psi^\dagger (r_2) | N, \lambda \rangle \]

\[ \omega_1 + i\delta - E_N^0 - E_{N+1}^0 \]

\[ - \sum_\alpha \langle N, 0 | \psi^\dagger (r_2) | N + 1, \alpha \rangle \langle N + 1, \alpha | \psi (r_1) | N, \lambda \rangle \]

\[ \omega_2 + i\delta + E_N^0 - E_{N-1}^0 . \]

(2)
As usual, $|N,0\rangle$ and $|N,\lambda\rangle$ are the exact ground state and plasmon/exciton excited state of the many-electron system, while the $\psi$ are the usual field operators. $\lambda$ represents a possible set of conserved quantum numbers. $G_{0,\lambda}$ satisfies the following homogeneous Bethe-Salpeter equation:

$$G_{0,\lambda}(1,2)=G(1,1')G(2',2) \times f(1',2';3',4')G_{0,\lambda}(4',1') ,$$

where $I=(r_1,\omega_1)$, etc. and integration over repeated indexes is assumed. $I$ is the irreducible particle-hole interaction, which contains the essential ingredients of the physical processes that we want to describe. For $I$, we consider the ladder approximation and neglect retardation effects, including the basic interactions described by the diagrams in Fig. 1. Upward pointing arrows describe particle states, downward pointing arrows describe hole states, the dashed line represents the bare particle-hole interaction and the double dashed line represents the screened particle-hole interaction. As is well known, since $I$ is an irreducible interaction, only diagram (b) must be screened (and vertex corrected).

To proceed, we now explicitly write, for $I$,

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

where $V_{\text{bare}}$ is the bare interaction and $W$ is the screened interaction. Considering the usual expansion for $f_\lambda$,

$$f_\lambda = X_{ph}\phi_p\phi_h + Y_{ph}\phi_p^*\phi_h^* ,$$

where $X_{ph}$ and $Y_{ph}$ are the forward-going and backward-going electron-hole amplitudes, respectively, whereas $\phi$ are quasiparticle wave functions, and inserting this expansion, together with the expression for $I$ in Eq. (2) and its solution in Eq. (1), we obtain, after a final frequency integration, the following matrix equation:

$$\begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = E \begin{pmatrix} X \\ Y \end{pmatrix} ,$$

where the matrices $A$ and $B$ are defined as

\begin{alignat*}{2}
A &= V_{\text{bare}} \\
B &= -W \delta
\end{alignat*}

FIG. 1. Graphical representation of $I$ as used in this work. It originates from all parts of the irreducible particle-hole interaction of the first order: bare Coulomb + bare exchange after the exchange part has been properly screened. According to the general rules for Feynman graphs part (a) must NOT be screened, because this would result in a reducible diagram (compare Ref. 10). Vertex corrections are not considered in this work.

FIG. 2. (a) Photoabsorption cross section per delocalized electron for jellium Na$_8$ in two different approximations: with a dashed line, the matrix-RPA-LDA (Ref. 16), which is equivalent to TD-LDA (Ref. 3); with a continuous line, the RPA-SE as developed in this paper. The blueshift of the main line results from the proper screening of the attractive part of the general irreducible particle-hole interaction (Refs. 10 and 11). For details, see main text. (b) Frequencies and oscillator strength of various particle-hole transitions in jellium Na$_8$ in three different approximations: crossing the so-called free response (meaning, that effects of the induced charge are neglected); the rest is the same as in Fig. 2(a), but without Lorentzian broadening. We chose this way of representation, in order to make more visible the redistribution of oscillator strength in the high-frequency part of the spectrum.
\[ A_{p,h} = (e_p - e_h) \delta(p, p') \delta(h, h') + \langle p' | h' \rangle, \]
\[ B_{p,h} = \langle p' | h' \rangle. \]

In Eqs. (7), (8), \( e_p (e_h) \), are quasiparticle (quasihole) energies, whereas the matrix elements between quasiparticle states read

\[ \langle p | h' \rangle = \int dr_1 \int dr_2 \int dr_3 \int dr_4 \rho_p^*(r_1) \phi_h^*(r_2) \times I(r_1, r_2, r_3, r_4) \phi_p(r_3) \times \phi_h(r_4). \]

Because these equations are formally identical to the RPAE equations, except for the residual particle-hole interaction, which has now a screened exchange term, we call the present results the RPA-SE equations. To our knowledge, this is the first time these equations have been explicitly obtained. Furthermore, we would like to point out that these equations are useful for the case of static screening, in which retardation effects are neglected. However, the modifications to be introduced in the present formalism, in order to incorporate dynamical screening effects are formally straightforward. We defer the study of dynamical screening effects to a future publication.

In order to implement the RPA-SE, we start from an independent-particle picture. Traditionally, the Hartree-Fock independent electron picture is the starting point. However, and since we are interested in studying the optical response of small clusters of simple metals, for which the Hartree-Fock approximation is known to provide a rather poor starting point, we start from a density-functional theory (DFT) scheme in the local-density approximation (LDA). Therefore, we compute the one-electron wave functions and energies in LDA to DFT, and correspondingly, the one-particle Green's functions. For the screened interaction \( W \), we compute it in Hedin's \( GW \) approximation, following the prescription proposed by Hybertsen and Louie. In this framework, instead of working out the complete self-consistent solution of the \( GW \) equations, one starts from the DLA approximation and carries out one interaction of the \( GW \) self-consistent scheme. This corresponds to

\[ W(r_1, r_2) = \frac{e^2}{|r_1 - r_2|} + \int dr_3 dr_4 \frac{e^2}{|r_1 - r_3|} \chi(r_3, r_4) \frac{e^2}{|r_4 - r_2|}, \]

for \( W \), where the density-density correlation function \( \chi \) is computed at the level of TDLDA. In general, \( \chi \) is a complex and energy-dependent function. In the static approximation, we take \( E = 0 \) and \( \chi \) becomes a real function.

Within TDLDA, or equivalently, the matrix RPA-LDA (see below), the general form for the interaction \( I \) is replaced by the so-called residual interaction. It reads, according to the previous definitions,

\[ K(r_1, r_2, r_3, r_4) = \delta(r_3 - r_2) \delta(r_4 - r_1) \left[ V_{\text{bare}}(r_1, r_2) + \frac{dV_{\text{XC}}}{dn} \delta(r_1 - r_2) \right] \]

\[ = \delta(r_3 - r_2) \delta(r_4 - r_1) \left[ \frac{e^2}{|r_1 - r_2|} + \frac{dV_{\text{XC}}}{dn} \delta(r_1 - r_2) \right]. \]

\[ \text{III. RESULTS AND DISCUSSION} \]

In this section, we apply the theory to a number of magic jellium clusters of Na, and compare them to other models, mainly to the old fashioned TDLDA. Figure 2(a) gives the photoabsorption cross section \( \sigma \) per delocalized electron for various models of calculation. As a reference, the dashed line gives the results of the matrix RPA-LDA. This curve is (of course) completely equivalent to the TDLDA. The only difference is that the latter calculates the dynamical polarizability and from this quantity the optical absorption, whereas the former calculates eigenvalues and eigenvectors, respectively, and from these quantities the optical absorption as described in detail by Yannouleas and Broglia. That means, each spectral line is Lorentzian broadened (here with the parameter \( \eta \) chosen to be 0.1 eV).

Next we solve the equations that mean that the irreducible particle-hole interaction is considered as given by Eq. (4), meaning that the attractive part of the interaction is properly screened, and the repulsive part is calculated.

\[ \text{FIG. 3. The same as Fig. 2(b), but for Na}_{20}. \]
Figure 4. The same as Fig. 2(b), but for Na_{58}. This result is interesting, because it shows clearly a fragmentation of the line shape in the collective region around 3 eV. This has not been found in the preceding study of Yannouleas, Vigezzi, and Broglia (Ref. 19).

Figure 5. The same as Fig. 2(a), but for Na_{92}. Microscopically, there is a fragmentation in the collective region. This, however, should be hard to resolve experimentally (which agrees with the interpretation of Ref. 19).

IV. CONCLUSIONS

The main qualitative features of the optical response of metal clusters are given by the overwhelming importance of the formation of the collective oscillation of all delocalized electrons: this phenomenon already present in the classical description of the optical properties persists to exist in a truly microscopic description, using the rather simple model of the TDLDa; therefore, it seems not too surprising that a true many-body solution of the problem, based on Feynman diagrams—in the way proposed by Sham and Rice—does not change our picture of the optical response very much. But nevertheless a study along this line has to be done, because there is still an ongoing controversy about the right description of the effects of exchange in this context.

For this reason, the marginal difference between TDLDa and the Bethe-Salpeter-Equation description is highly welcome, because the latter is rather accurate but numerically complex, whereas the former is numerically easy to do, but lacks a thorough justification. In this respect, we have a similar situation as we have with the so-called self-interaction correction, which has no sanctioning by any exact theorem, but turns out to be numerically equivalent to a quasiparticle calculation at the level of the \textit{GW} approximation (which is considered to be on a firmer theoretical basis). The general \textit{ph} interaction seems to be more important in clusters of other elements (e.g., rare gases, ionic species, or semiconductors), which will be studied next.

12Dynamical screening effects are known to be important for a correct description of excitonic effects. However, we will find that, in our case, the static screening provides a small contribution, and, therefore, we expect the dynamical correction to be unimportant in the present context.