Collective electronic excitations in small metal clusters

Susumu Saito

Department of Physics and Astronomy, Center for Fundamental Materials Research
and Cyclotron Laboratory, Michigan State University, East Lansing, Michigan 48824-1116
and Fundamental Research Laboratories, NEC Corporation,
34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan

George F. Bertsch and David Tománek
Department of Physics and Astronomy, Center for Fundamental Materials Research
and Cyclotron Laboratory, Michigan State University, East Lansing, Michigan 48824-1116
(Received 3 October 1990)

We extend the time-dependent density-functional theory by including the self-interaction correction (SIC) in order to determine collective electronic excitations in small metal clusters. We find that Mie plasmon frequencies of sodium clusters, obtained with SIC for jellium spheres, are in significantly better accord with experimental data than previous theories. We also find that the correct asymptotic behavior of the effective potential in SIC decreases the critical cluster size for the onset of Landau damping of the Mie plasmon.

A spherical-jellium-background model for simple metal clusters, combined with the local-density-approximation (LDA) in the density-functional-theory (DFT), has successfully explained magic numbers of stability observed in alkali-metal clusters by a shell structure reminiscent of the shell model in nuclear physics. In the spherical-jellium-background model, the positive-ion cores are replaced by a sphere with constant charge density, which is usually set equal to the bulk valence-electron density. The levels of interacting valence electrons, trapped in a Coulomb potential of the jellium sphere, show shell structure. This is one of the general features of Fermi systems such as electrons in an atom or nucleons in an atomic nucleus.

This simple metal—sphere picture triggered a renewed interest in collective excitations of valence electrons in metal clusters, namely, the plasmons. In the case of a classical metal sphere, the dipole excitation was first described by Mie and the corresponding resonance $\omega_{\text{Mie}}$ is independent of the sphere size. Recent photoabsorption—cross-section experiments have measured the Mie plasmon in free sodium clusters ($\text{Na}_N$, $N = 2 - 40$). The energy of the observed Mie resonance for closed-shell clusters ($\text{Na}_8$ and $\text{Na}_{20}$) is $\approx 2.5$ eV, which is considerably less than the classical value of 3.4 eV. The typical absorption linewidth is 0.4 eV, showing the presence of strong damping processes for this collective excitation.

Theoretical studies of the Mie plasmon within the spherical-jellium-background model have been performed using the time—dependent local-density—approximation (TDLDA). Calculated photoabsorption cross sections for $\text{Na}_8$ and $\text{Na}_{20}$ give Mie plasmon peaks around 2.7 eV. While this result represents a shift of the classical value in the correct direction, this energy is still larger than the observed values. Also, TDLDA for jellium spheres predicts the onset of Landau damping only for larger cluster sizes ($N \geq 92$). Note, however, that the authors of Ref. 7 found a splitting of the Mie state even in $\text{Na}_{20}$, using a different method to solve the TDLDA equations.

In this paper, we address these problems using TDSIC, a time—dependent density-functional theory with self—interaction correction (SIC). We show that TDSIC lowers Mie plasmon energies of closed—shell clusters ($\text{Na}_N$; $N = 2, 8, 18, 20, 34, \text{and} 40$) (Ref. 10) and brings them into much better accord with experiments than TDLDA. In addition, TDSIC yields much more structure in the photoabsorption spectrum, producing Landau damping at much smaller cluster sizes.

We believe that the local-density approximation is primarily responsible for the overestimate of the plasmon frequency. This is seen in the following argument. In finite systems with $N$ electrons, each electron is screened by the other $N - 1$ electrons. However, in LDA (and consequently also in TDLDA), each electron is screened by all $N$ electrons including itself. This overscreening is more serious in smaller systems, yielding considerably smaller static polarizabilities in metal clusters. Actually, the inclusion of a self—interaction correction, which removes the overscreening problem in LDA, has been shown to give reasonable static polarizabilities for sodium clusters within the spherical jellium model. Since the photoabsorption cross section, which is dominated by the Mie plasma resonance, is related to the static polarizability through the Kramers—Kronig relation, the overestimate of the Mie plasmon energy should be related to the underestimated value of the static polarizability. This is consistent with the finding that TDLDA for spherical jellium gives systematically smaller static polarizabilities than the experiment.

In LDA, one—particle states in the self—consistent Kohn—Sham theory are the eigenstates of a hypothetical system of noninteracting quasielectrons. Recent studies of dressed one—electron Green’s functions, based on the GW approximation, have demonstrated that the LDA wave functions are a very good representation of quasi—
particle wave functions in the bulk of solids as well as in finite systems. However, the LDA ionization potentials are less satisfactory because of an incorrect asymptotic behavior of the potential. The self-interaction correction, which corresponds to the removal of the self–Hartree potential and the self–exchange-correlation potential, gives the correct asymptotic behavior $V \propto r^{-1}$ for $r \to \infty$ (instead of the incorrect exponential decay in LDA) for spherical jellium and does not affect the wave functions to a large extent. Consequently, SIC is expected to give better excitation energies below the ionization threshold, ensuring a better density-density response function which determines the photoabsorption cross section. A nontrivial complication of SIC is the fact that the effective SIC potential differs from state to state. Therefore, unlike in LDA, an inclusion of time dependence in SIC is not straightforward and has not been done.

In the present work, the effective potential $V_{\text{eff}}^\text{LDA}(r)$ in the Kohn–Sham equations is replaced by the SIC effective potential for the particle in the highest occupied state, $V_{\text{eff}}^\text{SIC}(r) = V_{\text{eff}}^\text{LDA}(r) - V_{\text{H}}[\rho_{\text{HO}}(r)] - V_{\text{xc}}[\rho_{\text{HO}}(r)]$.  

Here, $V_{\text{H}}[\rho_{\text{HO}}(r)]$ and $V_{\text{xc}}[\rho_{\text{HO}}(r)]$, respectively, are the Hartree and exchange-correlation potential associated with the density $\rho_{\text{HO}}$ of the electron in the highest occupied state. The LDA effective potential $V_{\text{eff}}^\text{LDA}$ is the sum of the Coulomb potential of the positive jellium background and the total electron density, and the exchange-correlation potential. This potential $V_{\text{eff}}^\text{SIC}$ will be used not only for the highest occupied state, but also for all the other states. The reasoning behind this approximation is that the highest occupied states have the largest polarizability and influence the dielectric response of clusters to the largest extent. Since the new potential is still local and state independent, the extension from SIC to TDSIC is straightforward, similar to the extension from LDA to TDLDA. In spite of its simplicity, $V_{\text{eff}}^\text{SIC}(r)$ still retains important properties for calculating the Mie plasmon. The correct asymptotic behavior at $r \to \infty$, which assures a better description of excitations to unoccupied states, is guaranteed for all states. Moreover, the ionization potential, which is given in DFT (and consequently also in SIC) by the energy of the highest occupied state, is expected to be better than in LDA. Even though the Mie plasmon is a collective motion of all electrons, the most important component is the excitation from the highest occupied state to the lowest unoccupied state, which is described better in TDSIC than in TDLDA.

In TDSIC, the independent–particle density–density response function is given by

$$
\chi^0(r, r'; \omega) = \sum_i \frac{\psi_i(r')\psi_i^*(r)}{\epsilon_i + \omega} G(r, r'; \epsilon_i + \omega) + \frac{\psi_i(r)\psi_i^*(r')}{\epsilon_i - \omega} G^*(r, r'; \epsilon_i - \omega),
$$

where $\psi_i$ and $\epsilon_i$ are the wave functions and energies obtained using SIC, and $G$ is the SIC (retarded) one-electron Green’s function. Since the system has a spherical symmetry, $G$ is given by the product of the two different solutions of the boundary–value problem of the Schrödinger equation with $V_{\text{eff}}^\text{SIC}(r)$. One of the solutions should be regular at $r \to 0$ and the other should be regular at $r \to \infty$, with outgoing–wave behavior for the retarded $G$. In the calculation of the latter solution, the long–range Coulomb tail of $V_{\text{eff}}^\text{SIC}$ must be treated adequately.

The density–density response function $\chi$ is related to $\chi^0$ by

$$
\chi(r, r'; \omega) = \chi^0(r, r'; \omega) + \int \! dr'' \int \! dr''' \chi^0(r, r'''; \omega) K(r'', r''') \chi(r''', r'; \omega).
$$

The kernel $K$ is the functional derivative of the effective potential, given by

$$
K(r, r') = \frac{\delta V_{\text{eff}}(r)}{\delta \rho(r')}. \tag{4}
$$

The expression for the TDLDA kernel $K^\text{LDA}$ involves the LDA effective potential $V_{\text{eff}}^\text{LDA}$. Since the potential is modified by SIC, the kernel should be changed accordingly. However, for the sake of simplicity, we did not use the definition in Eq. (4), but simply reduced the interaction by a state–independent factor. Our model for $K^\text{SIC}$ is

$$
K^\text{SIC}(r, r') = \frac{N - 1}{N} K^\text{LDA}(r, r'). \tag{5}
$$

In Table I, the ionization potentials for Na$_N$ clusters, obtained using SIC for spherical jellium, are listed together with the results obtained from LDA and GW, and with experimental values. Our results are based on the value $\rho_{\text{pel}} = 3/4\pi r_s^3$ for the charge density of the constant jellium background corresponding to $r_s=4$ a.u. The absolute values of the energies of the highest occupied state in GW for spherical jellium are very close to LDA values for the total–energy differences between Na$_N$ and Na$_N^+$ in the ground state. These values are also believed to be close to the ideal ionization potentials of the jellium spheres.

It has been known that the LDA highest occupied state is too shallow to give correct ionization potentials, and that the full state–dependent SIC calculation gives much better ionization potentials. As can be seen from Table I, the present simplified SIC also works well, giving better ionization potentials than LDA. This improvement is attributed to the removal of the static self–screening in LDA by SIC. In Fig. 1, we have shown the SIC effective potential in Na$_8$. This potential is considerably deeper than the LDA effective potential, and yields increased binding energies for occupied states.
In order to investigate the manifestation of the Mie plasmon in the photoabsorption spectrum, we calculate the dynamical polarizability α(ω) = −e² ∫ dr dr' zχ(r, r'; ω)z', where ω Imα(ω) is proportional to the photoabsorption cross section. In Fig. 2, we show our results for Imα(ω) in Na₈ and Na₄₀, obtained using TDLDA and TDSIC. In the case of Na₈, TDSIC gives a much richer structure in the high-energy region of the polarizability than TDLDA. The origin of this richer spectrum is the long-ranged Coulomb tail in the effective SIC potential which “pulls down” discrete excitations from the continuum. Also, the TDSIC spectrum shows a prominent peak around 2.5 eV. We find this peak to be at least one order of magnitude stronger than others and regard it as a Mie plasmon peak. The peak at 1.7-eV, which is roughly 10 times weaker than that at 2.5 eV (note the logarithmic scale in Fig. 2), is also present in the spectrum when we compute the absorption using χ² instead of χ. Thus the 1.7-eV feature represents a noncollective excitation, specifically, from the cluster’s highest-occupied state to its second lowest unoccupied state.

The energy of the Mie resonance is lower than that obtained using TDLDA, a consequence of the result that several of the lower unoccupied states experience a stronger shift to larger binding energies than the highest occupied state. The effect of SIC on the individual levels can be analyzed using Eq. (1). The self–Hartree term, which dominates the net shift towards higher binding energy, is partly compensated by the self-exchange correlation term. The self–Hartree correction of the highest occupied states is very efficiently reduced by the exchange-correlation correction which is local and works mainly inside the jellium sphere. For the lower unoccupied states, on the other hand, the reduction of the

<table>
<thead>
<tr>
<th>Cluster size</th>
<th>Ionization potential (eV)</th>
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</thead>
<tbody>
<tr>
<td>N</td>
<td>LDA</td>
</tr>
<tr>
<td>1</td>
<td>5.1</td>
</tr>
<tr>
<td>2</td>
<td>3.3</td>
</tr>
<tr>
<td>8</td>
<td>3.3</td>
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</tr>
<tr>
<td>34</td>
<td>3.1</td>
</tr>
<tr>
<td>40</td>
<td>2.8</td>
</tr>
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<td></td>
</tr>
</tbody>
</table>

*Reference 15.
*Reference 18.

FIG. 1. SIC effective potential V_{eff}^{SIC} (solid line) for Na₈, with the correct asymptotic behavior V ∝ r⁻¹ (dashed line). The dotted line is the LDA effective potential, V_{eff}^{LDA}. The vertical solid line shows the radius of the jellium sphere.

FIG. 2. Imaginary part of the dynamical polarizability log₁₀[|Imα(ω)|/R²], shown on a logarithmic scale for (a) Na₈ and (b) Na₄₀. The smooth curves have been determined by including a small imaginary part in the frequency ω. The TDSIC results, given by the solid line, have been shifted by +7 and the TDLDA results, given by the dashed line, have been shifted by +3 for the sake of better comparison. The radii of the jellium spheres are R(Na₈)=8.00 a.u. and R(Na₄₀)=13.68 a.u. The ionization thresholds are shown by vertical arrows.
(relatively smaller) self–Hartree term by the exchange-correlation correction is far less significant. Hence the net shift towards higher binding energies is larger for the lower unoccupied states than for the highest occupied states. The consequence of this effect is a net red shift of the excitation energies. This results in a larger static polarizability and a smaller Mie plasmon energy.

In the case of Na_{N0}, the TDSIC spectrum shows a dense band of strong peaks at 2.0–3.5 eV, and the identification of the Mie plasmon from the “strongest resonance” is impossible. (Lower excitations around 1 eV are again identified as particle–hole pair excitations.) This rich spectrum obtained by TDSIC is quite different from the TDLDA result for the same cluster. The inadequate treatment of the Coulomb potential in TDLDA results in a rather clear peak at 2.6 eV corresponding to the Mie plasmon. The lowering of the unoccupied states by the Coulomb tail of \( V_{\text{eff}} \) in TDSIC also results in the onset of Landau damping at much smaller cluster sizes than in TDLDA.

In Table II, we present Mie plasmon energies calculated by TDLDA and TDSIC. In Na_{2}, TDSIC gives a moderate red shift of the Mie plasmon as compared to TDLDA.\(^{20}\) In Na_{8}, the self–interaction correction yields a significant red shift of the plasmon from the TDLDA value, resulting in a very good agreement with the experiment. The tendency of TIC to red shift TDLDA values for the Mie resonance persists also in the larger clusters. For larger Na_{N} \((N > 8)\), the specific form of the kernel \([K = K_{\text{LDA}} \text{ or } K = K^{\text{SIC}}] \) in Eqs. (3) and (5) is found to play only a negligible role.

In conclusion, we have proposed TDSIC, the time–dependent density-functional theory with self-interaction correction. This formalism gives Mie plasmon energies of Na_{N} which are in much better agreement with experimental data than the previous quantitative first–principles theory, TDLDA. In general, SIC corrects the self–screening present in LDA, yields the correct asymptotic behavior of the effective potential and increases the polarizability of clusters. The corresponding time–dependent theory TDSIC lowers the energy of the Mie plasmon for all cluster sizes. In addition, TDSIC is found to decrease the critical cluster size for the onset of Landau damping of the Mie plasmon.

The authors acknowledge useful discussion with Dr. Yongsheng Li and Yang Wang. This research was partly supported by the National Science Foundation under Grant No. PHY-87-14432.

\( \text{TABLE II. Mie plasmon energies (eV) of Na}_{N} \text{ clusters in the spherical jellium model. Theoretical values obtained using TDLDA and TDSIC are compared to experimental data. For Na}_{20}, \text{ the calculated values are the average of three (two) strong peaks in TDSIC (TDLDA). In Na}_{40}, \text{ the strong Landau damping makes an identification of the Mie plasmon impossible (see Fig. 2).} \)

<table>
<thead>
<tr>
<th>Cluster size</th>
<th>Mie plasmon energy (eV)</th>
<th>TDLDA</th>
<th>TDSIC</th>
<th>Expt.*</th>
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</thead>
<tbody>
<tr>
<td>N</td>
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<td></td>
<td></td>
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<td>40</td>
<td></td>
<td>2.56</td>
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</table>

*Reference 3.*

10. In the case of open–shell clusters, the spheroidal–sphere model works better [see K. Clemenger, Phys. Rev. B 32, 1359 (1985)]. In this paper, however, we study closed–shell clusters where the spherical–jellium–background model is applicable.
12. P. Stampfl and K. H. Bennemann, Phys. Rev. A 39, 1007 (1989). The self–screening problem occurs not only in TDLDA, but is also present in more phenomenological models such as the Thomas–Fermi theory.
20. In the case of Na_{2}, this red shift is likely to be enhanced by a further increase of the static polarizability due to discrete atomic structure [I. Moullet and J. L. Martins, J. Chem. Phys. 92, 527 (1990)].