N-block separable random phase approximation: dipole oscillations in sodium clusters and $C_{60}$ fullerene

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Received 8 March 2016, revised 19 June 2016
Accepted for publication 7 July 2016
Published 10 August 2016

Abstract

We generalize the schematic model based on the Random Phase Approximation (RPA) with separable interaction, to a collection of subspaces of ph excitations which interact with different coupling constants. This ansatz notably lowers the numerical effort involved, by reducing the RPA eigenvalue problem to a finite small dimensional system of equation. We derive the associated dispersion relation and the normalization condition for the newly defined unknowns of the system. In contrast with the standard separable approach, the present formalism is able to describe more than one collective excitation even in the degenerate limit, giving also access to the nature of the resonance. The theoretical framework is tested investigating the dipolar oscillations in various neutral and singly charged sodium clusters and $C_{60}$ fullerene with results in good agreement with full RPA calculations and experimental data. It is proven that the 40 eV resonance present in photoabsorption spectra of $C_{60}$ is a localized surface plasmon.

Keywords: random phase approximation, separability, cluster, fullerene

1. Introduction

Recently [1, 2] we have investigated the collectivity of the Giant Dipole Resonance and of the low-lying modes (Pigmy Dipole Resonance) in nuclear systems using the separable RPA. In contrast with the standard schematic model [3] which employs separable residual interaction with a single specific coupling constant between pairs of ph excitations, we have assumed the existence of two subsystems of particle-hole states and, consequently, three distinct coupling constants.

In the present work this approach is generalized to a variable number of subsystems of particle-hole pairs, allowing us to describe an even higher number of collective resonances—a feature which is relevant to finite quantum systems such as (metallic) clusters. The photoabsorption/photoionization spectra of clusters has been intensively studied in the past three decades from both an experimental and a theoretical point of view [4–8]. The most pregnant phenomena in the optical response of (metal) clusters, is the surface plasmon. This represents a dipolar motion of the electron cloud against the ionic background, similar with the Goldhaber-Teller description of the Giant Dipole Resonance in nuclei [9]. This motion induces density oscillations at the surface of the electronic cloud and thus, the surface nature of the resonance. Another collective phenomenon is the so called volume plasmon which, from a macroscopic view is characterized by density variations inside the cluster volume as in the Steinwedel-Jensen model [10].

These are gross properties of the optical spectra, exhausting high fractions of the total sum rule. But varying the number of atoms, the shell effect begin to manifest [6]. This is reflected directly in the shape of clusters finding spherical magic clusters ($n = 8, 10, 20, 40, 58, 92, etc$) and many deformed ones in between. Moreover, for clusters with
a small number of atoms, the details of the ionic background become important. All these deviations from the spherical symmetry affect the optical spectra allowing for relevant single particle excitations or fragmentations of the collective surface plasmon, the latter being connected with the phenomenon of Landau damping.

Unlike in nuclear physics, where Hartree–Fock (HF) is the most used microscopic theory, the dynamics of electrons in clusters is usually investigated by means of the Density Functional Theory (DFT) [6, 11, 12] which is implemented through the Kohn-Sham equations (KS) [13]. The extension to the time-dependent case describes the properties of excited states and its small amplitude limit represents the correspondent of the HF derived RPA.

Even though RPA can be easier to implement than the full propagation of time-dependent-HF or time-dependent-DFT, it still poses a difficult numerical task. This is reflected in the dimension of the space of single particle excitations, given the fact that for each pair of $ph$ states, two 6D integrals should be computed. The difficulty arises especially in deformed clusters, where the space of the single particle states lacks the degeneracy associated with spherical symmetry.

To overcome such numerical challenges, in recent decades there has been active research into the art of simplifying RPA methods. The lowest level of approximation is given in the frame of sum rule techniques [14] where a single resonance is described. A more pertinent description is achieved within the local RPA method [15] where a set of local operators is used to describe an equal set of collective resonances, but the Landau damping features are lost. The original separable ansatz [3] is used in cluster physics as the vibrational potential model [14, 16]. This has the main disadvantages that only one collective excitation is obtained and the natural fragmentation of the surface plasmon is not properly described. A more refined method is provided by the self-consistent separable RPA (SRPA) [17, 18] which combines the idea of many local operators with the separability ansatz of the residual interaction.

In this work we generalize the separability of the residual interaction in the frame of DFT-LDA using a single operator but many coupling constants prescribed by $N$ blocks of $ph$ excitations, method which will be referred to as $N$ Block Separable RPA (N-BSRPA). Our formalism has many similar points with the one developed in [18], but, as we shall see, the interpretations are fundamentally distinct. While SRPA describes a system of coupled collective motions, N-BSRPA accounts for a collection of coupled subsystems of oscillators.

The paper is organized as follows: in section 2 a short derivation of DFT derived RPA is given and the formalism of N-BSRPA is developed. In section 3 the formalism is applied for some sodium clusters and $C_{60}$ fullerene, leading to results in good agreement with full RPA predictions or experimental results. Furthermore, in this framework we confirm once again the debated interpretation [19–22] of the 40 eV resonance [22–25] present in $C_{60}$ photoabsorption spectra in terms of two out-of-phase surface modes.

2. Theory

2.1. RPA from DFT

The time-dependent DFT [26] within the adiabatic local density approximation (ALDA) [27] can be represented through the Kohn-Sham equations, which for a system of electrons described by single particle orbitals $\{\phi_j(\mathbf{r}, t)\}$ read:

$$\hat{h}\{\rho(\mathbf{r}, t)\}\phi_j(\mathbf{r}, t) = i\hbar\partial_t\phi_j(\mathbf{r}, t),$$

$$\rho(\mathbf{r}, t) = \sum_{j \in occ} |\phi_j(\mathbf{r}, t)|^2.$$  \hspace{1cm} (1)

$j \in occ$ indexes the occupied single particle states, $\rho(\mathbf{r}, t)$ is the total particle density and $\hat{h}\{\rho(\mathbf{r}, t)\}$ is a mean field Hamiltonian operator incorporating, besides the kinetic term, the Coulomb interaction between electrons, a local potential for the exchange-correlation effects and an external potential. Since we are interested in the normal modes of the electron system, we consider that the external potential is given only by the Coulomb interaction between electrons and ions.

In the stationary case, the KS equations become eigenvalue problems $\hat{h}_0[\rho_0(\mathbf{r})]\varphi_j(\mathbf{r}) = \varepsilon_j\varphi_j(\mathbf{r})$. Each orbital can be expanded around its stationary value $\phi_j(\mathbf{r}) = (\varphi_j(\mathbf{r}) + \delta\phi_j(\mathbf{r}, t))e^{-i\varepsilon_jt/\hbar}$ and with this expansion we can linearize the density and the Hamiltonian as:

$$\delta\rho(\mathbf{r}, t) = \sum_{j \in occ} \varphi_j^*(\mathbf{r})\delta\phi_j^\dagger(\mathbf{r}, t) + c.\ c.\ c.,$$

$$\hat{h}[\rho] = \hat{h}_0[\rho_0] + \frac{\delta h}{\delta \rho} |_{\rho_0} \delta \rho. \hspace{1cm} (4)$$

While in normal modes, $\delta\phi_j$ must have oscillating behaviour, so we expand it in the basis of both occupied and unoccupied single-particle states with harmonic coefficients:

$$\delta\phi_j(\mathbf{r}, t) = \sum_{\mu \in all} \varphi_{\mu j}(\mathbf{r})X_{\mu j} e^{-i\varepsilon_jt/\hbar} + Y_{\mu j}^* e^{i\varepsilon_jt/\hbar}. \hspace{1cm} (5)$$

Replacing the linearised forms (3) and the expansion (5) of $\delta\phi_j(\mathbf{r}, t)$ in equation (1) and integrating the equation after multiplication with some $\varphi_{\nu i}$, we obtain the usual form of the RPA eigenvalue equations:

$$\varepsilon_j X_{\mu j} + \sum_{\nu} (A_{\nu j}X_{\nu j} + B_{\nu j}Y_{\nu j}) = E^{(\nu)}X_{\nu j}, \hspace{1cm} (6)$$

$$\varepsilon_j Y_{\mu j} + \sum_{\nu} (B_{\nu j}X_{\nu j} + A_{\nu j}Y_{\nu j}) = -E^{(\nu)}Y_{\nu j}, \hspace{1cm} (7)$$

with $\sum_{\nu}(|X_{\nu j}|^2 - |Y_{\nu j}|^2) = 1$ as normalization condition. In deriving the above equations, we used the compact notations $X_{\mu j} \equiv X_\mu$, $Y_{\mu j} \equiv Y_\mu$, $\varepsilon_\mu - \varepsilon_j \equiv \varepsilon_\mu$, $A_{\nu j} \equiv \langle \varphi_{\nu j}|\hat{h}|\varphi_{\nu j}\rangle$, $B_{\nu j} \equiv \langle \varphi_{\nu j}|\delta\hat{h}\delta\rho|\varphi_{\nu j}\rangle$. The superscript $(k)$ labels the solutions of the eigenvalue problem. For legibility we shall suppress this notation whenever possible. In literature, the results of this derivation are also known as the linearized TDDFT. More detailed discussions and related derivations can be found in literature [28–31].
It might seem that, unlike in the HF derived RPA, the system of equation (6) describes transitions from occupied states into other occupied states, fact which violates the Pauli principle, but in practice, since these terms cancel each other, we will set them to 0. While in the standard RPA the residual two-body interaction is the difference between direct and exchange terms, in the DFT-LDA derived RPA it is given by the kernel $\delta h(r)/\delta \rho(r')$ which will be detailed later.

The system of equations (6) can be written in matrix notation as:

$$
\begin{pmatrix}
\hat{A} & \hat{B} \\
-\hat{B}^* & -\hat{A}^*
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix}
=
\begin{pmatrix}
\hat\xi_-(E) & 0 \\
0 & \hat\xi_+(E)
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix}
$$

(8)

where we defined the RPA matrices $\hat{A} = \{A_{ij}\}$, $\hat{B} = \{B_{ij}\}$, $\hat\xi_\pm(E) = \{\delta_{ij} (E \pm \epsilon_i)\}$ and the vectors $X = \{X_i\}$, $Y = \{Y_j\}$.

2.2. Block-separable ansatz

The standard separable ansatz states that for all $(ph, p'h')$ pairs, the two-body matrix elements can be factorized in terms of an one-body transition operator $\hat{q}$: $A_{ph,p'h'} = \lambda(Q_{ph}^{ph} Q_{p'h'})$, where $Q_{ph} = \{\langle \phi_j | \hat{q} | \phi_h \rangle\}$. Already in [1] we have relaxed this condition using three different coupling constants. We generalize this result to $N$ blocks of $ph$ excitations. In order to achieve such a description in an elegant manner, in the following we will adopt the matrix notation with compact indexes $i = ph$ and $j = p'h'$.

Let us consider the unique set of coupling constants $\lambda_{ij} = A_{ij}/(Q_{ij}^{ph} Q_{ij})$. We construct the set of matrices and vectors:

$$
\hat{\Lambda} = \{\lambda_{ij}\}, \quad \hat{\mathbf{Q}} = \{Q_{ij}\},
$$

$$
\Xi = \{\hat{\mathbf{Q}}^* \hat{\mathbf{Q}}\}, \quad \hat{\chi}(E) = \{\hat{\mathbf{Q}}^{-1} [\hat{\xi}_-(E) - \hat{\xi}_+(E)]\},
$$

where $\hat{\Lambda}$ is the real and symmetric matrix of coupling constants and $\hat{\mathbf{Q}}$ the diagonal matrix of $ph$ strengths. The $\Xi$ vector hides more physical meaning being related to the transition amplitude for the $k$th excited state $(0|\hat{q}|k) = |\Xi(k)| = \sum_{\{\xi\}} \Xi^{(k)} \cdot$ The element of the diagonal matrix $\hat{\chi}_i(E) = 2|\hat{\mathbf{Q}}^{-1} \hat{\xi}_i(E)|$ can be identified as the independent particle response function for a single $i = ph$ state.

Using the separable form of the interaction matrices $\hat{\Lambda} = \hat{\mathbf{Q}} \hat{\Lambda} \hat{\mathbf{Q}}$, $\hat{\mathbf{B}} = \hat{\mathbf{Q}} \hat{\Lambda} \hat{\mathbf{Q}}$ we can rewrite the system of equations (8) as:

$$
\begin{pmatrix}
\hat{\xi}_-^{-1} & 0 \\
0 & \hat{\xi}_+^{-1}
\end{pmatrix}
\begin{pmatrix}
\hat{\mathbf{Q}}^* \hat{\Lambda} \hat{\mathbf{Q}} & \hat{\mathbf{Q}} \hat{\Lambda} \hat{\mathbf{Q}} \\
-\hat{\mathbf{Q}}^* \hat{\Lambda} \hat{\mathbf{Q}} & -\hat{\mathbf{Q}} \hat{\Lambda} \hat{\mathbf{Q}}
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix}
=
\begin{pmatrix}
X \\
Y
\end{pmatrix}
$$

Multiplying both sides with $(\hat{\mathbf{Q}}^* \hat{\Lambda} \hat{\mathbf{Q}})$ we obtain the simplified form:

$$
\hat{\chi}(E) \hat{\Lambda} \Xi = \Xi.
$$

(9)

Note that this relation is equivalent with the original RPA equations (6) and since we defined the coupling constants for each $ph, p'h'$ pair, no approximation has been made so far. The dimensionality of the problem has been halved, but the new dispersion relation is complicated enough, being contained in the condition of singular matrix:

$$
det(\mathbf{I} - \hat{\chi}(E) \hat{\Lambda}) = 0.
$$

(10)

Let us further define the set of all single particle excitations as $\pi = \{\{ph\}\}$ and decompose it in $N$ subset called blocks $\pi = \bigcup_{n=1}^{N} \pi_n$. We now employ the generalized concept of separability. We assume that pairs of particle-hole states interact with different coupling constant corresponding to the blocks they belong to $\lambda_{ij} \equiv \lambda_{nm}$, $\forall i \in \pi_n, j \in \pi_m$, $\forall n, m = 1, N$. With this assumption one can rearrange the elements from (9) such that the $\hat{\Lambda}$ matrix becomes an array of constant blocks:

$$
\hat{\Lambda} = \begin{pmatrix}
\lambda_{11} & \lambda_{12} & \cdots & \lambda_{1N} \\
\lambda_{21} & \lambda_{22} & \cdots & \lambda_{2N} \\
\vdots & \vdots & \cdots & \vdots \\
\lambda_{N1} & \lambda_{N2} & \cdots & \lambda_{NN}
\end{pmatrix},
$$

(11)

where $\lambda_{nm}$ is a matrix with all elements 1 and dimension $|\pi_n| \times |\pi_m|$ with $|\pi_n|$ being the cardinality of the set $\pi_n$. Thus, the system (9) is reduced to a $N$-dimensional system (with the same form), in which the quantities involved are now defined as sums over $ph$ excitations in the same block $\lambda_{nm}(E) = \sum_{j \in \pi_n} \lambda_{ij}(E), \Xi_n = \sum_{j \in \pi_n} \Xi^{(j)}, |\Xi^{(j)}| = \delta_{nm} \sum_{j \in \pi_j} |Q_{ij}^2|$, $n = 1, N$.

Using the normalization of the initial RPA $\sum_{i,j} |(\mathbf{X}^j)^i|^2 = |\mathbf{X}^j|^2 = 1$ and the dependency between $\Xi$ and $\{\mathbf{X}, \mathbf{Y}\}$ we can derive a normalization condition for the solutions of (9). The complete set of equations prescribed by our formalism:

$$
\hat{\chi}(E) \hat{\Lambda} \Xi = \Xi,
$$

$$
det(\mathbf{I} - \hat{\chi}(E) \hat{\Lambda}) = 0,
$$

$$
\Xi(\partial_E \hat{\chi}^{-1}(E)) \Xi = 1.
$$

(12)

Since $\hat{q}$ is the transition operator, the total response function (normalized to the sum rule) can be written:

$$
S(E) = \sum_k \frac{|\Xi^{(k)}|^2}{m_{l}(q)} \mathcal{L}(E, E^{(k)}, \Gamma^{(k)}),
$$

(13)

where $\mathcal{L}(E, E^{(k)}, \Gamma^{(k)}) = 2E^{(k)} \Gamma^{(k)} (E - E^{(k)})^2 + E^{2(\Gamma^{(k)})^2}^{-1}$ is the Lorentzian broadening of the delta function with some phenomenological width $\Gamma^{(k)} \ll E^{(k)}$. The $m_{l}(q)$ term is the first moment of the dynamic structure factor corresponding to the $\hat{q}$ operator and obeying the TKR sum rule [32].

From a second quantization perspective, the same results can be obtained imposing the separability of the residual interaction:

$$
\delta h = \frac{1}{2} \sum_{n,m} \lambda_{nm} s^{(n)} \hat{c}^+_m s^{-}_m,
$$

(14)
\[ \hat{\xi}_n = \sum_{j \in \pi_n} Q_j \hat{\delta}_j, \]

where \( \hat{\delta}_j \equiv \hat{a}_j ^\dagger \hat{a}_j \) is the fermionic creation operator. It can be shown that the vector \( \Xi \) is related to the matrix elements of the operator \( \hat{\xi}_n \) by \( \Xi^{(k)} = \langle 0 | \hat{\delta}_j | k \rangle \), and that the operators \( \hat{\xi}_n \) verify the anti-commutation relation \( \{ \hat{\xi}_n^\dagger, \hat{\xi}_m \} = \delta_{nm} \sum_{i \in \pi_n} \langle Q_{i} \rangle ^2 = \langle Q \hat{\xi}_m \rangle ^2 \).

We stress out that even if our results are very similar to the ones in [1] (section II D), the physical picture is completely different: while they use a set of operators \( \{ \hat{\xi}_n \} \) projected on the \( \pi \) space of \( \phi \) excitations, we use a single operator \( \hat{q} \) projected on a set of \( \{ \pi_n \} \) spaces. Consequently, their coupling constants represent a measure of the coupling between different collective motions, while in this work, \( \lambda \) is a measure of the interaction between two blocks. The similarities arise from the mathematical apparatus which is inherently the same.

Let us now emphasize the main advantages of \( N \)-BSRPA:

i. The dimension of the original problem \( 2 \text{occ} \times \text{unocc} \) (which is infinite in principle) can be dramatically reduced to a linear system with dimension \( N \).

ii. The number of solutions of the dispersion relation (10) is preserved since the latter can be written as an \( 2 \text{occ} \times \text{unocc} \) real polynomial in \( E \). The rank-nullity theorem prescribes one \( \Xi^{(k)} \) solution for each \( E^{(k)} \) excitation energy.

iii. The phenomenon of Landau damping is reproduced due to the presence of single particle effects in the block response function \( \chi_n(E) \).

iv. The TKR [32] sum rule is recovered in block form by the solutions of (9):

\[
m_q(q) = \sum_i |Q_{i}|^2 \xi_i = \sum_k |\Xi^{(k)}|^2 E^{(k)} = \langle [\hat{q}^\dagger, [\hat{h}, \hat{q}]] \rangle.
\]

Recognizing that the elements of \( \hat{\chi} \) are individual response functions for each block \( \pi_n \) and having in mind the form of the residual interaction (14) we support the idea that the present formalism models a collection of coupled sub-systems of oscillators.

2.3. Prescription of blocks and coupling constants

While the present formalism offers a heavily simplified alternative to RPA calculations, it is not complete since it does not prescribe how to choose the \( \pi_n \) blocks or how to compute the coupling constants \( \lambda_{nm} \). The problem originates in the absence of any mathematical proof that the long-range Coulomb interaction or some functional form of the exchange-correlation potential would have separable form, either for HF or KS orbitals. Therefore, the straight way would be to compute the \( \lambda_{ph,p'h'} \) from \( A_{ph,p'h'} \) and \( Q_{ph} \) and to define the blocks from the distribution of coupling constants. But since the main point of the present model is to avoid the calculation of \( A_{ph,p'h'} \) terms, this path is of no interest.

In order to overcome this issues, we first make a supplementary prescription for the blocks: \( \pi_n = \{ \text{ph} | p \equiv \phi \in \gamma_p \} \) where \( \gamma_p = \{ \phi \} \). In words, we define a block as all the \( \phi \) excitations which have as particle an occupied state from some predefined set of ground state orbitals \( \gamma_p \) which we will call single particle image of block \( \pi_n \). This choice allows for (and is motivated by) a mapping between our problem and a single particle picture.

With this mapping we can compute an approximative expression for the coupling constants. For that, we use the second order variation of the block-block potential energy

\[
E_{pot}^{n,m} = \int d\mathbf{r}\hat{\rho}_n(\mathbf{r}) \frac{\delta^2 H}{\delta \hat{\rho}_m \delta \hat{\rho}_n}(\mathbf{r}),
\]

where we define the image density \( \hat{\rho}_n(\mathbf{r}) \equiv \lambda_{nm} \hat{\rho}_m(\mathbf{r}) \). After applying the formal variation and using the anzatz, in terms of linear variations \( \delta \hat{\rho}_n(\mathbf{r}) \equiv \lambda_{nm} \hat{\rho}_m(\mathbf{r}) \), we find:

\[
\delta^2 E_{pot}^{n,m} = \lambda_{nm} \delta Q_n \delta Q_m
\]

\[
\delta Q_n = \sum_{i \in \pi_n} \int d\mathbf{r} \delta \hat{\rho}_i(\mathbf{r}).
\]

The equation (16) tells us that the coupling constants between two blocks \( \pi_n \) and \( \pi_m \) can be obtained knowing the variation of the interaction energy and the \( \hat{q} \) observable from some small variation of the densities \( \delta \hat{\rho}_n \). But the latter is dependent on the RPA solutions. This problem can be removed considering that the density variations \( \delta \hat{\rho}_n \) are generated by the transition operator \( \hat{q} \). In this case \( \delta \hat{\rho}_n = \hat{q} \rho_n \) [33], where \( \tilde{\rho} \equiv [\hat{h}, \hat{q}] \). Restricting ourselves to null-laplacian operators \( \hat{q} \equiv r = r Y_m(\Omega) \) and using some integration by parts, we can show that:

\[
\delta^2 E_{pot}^{n,m} = \int d\mathbf{r} \nabla^2 \rho_n(\mathbf{r}) \nabla \Phi_m(\mathbf{r}),
\]

\[
\Phi(r) = \int d\mathbf{r} \delta \frac{\delta \hat{h}}{\delta \hat{\rho}}(\mathbf{r}) \rho_m(\mathbf{r}),
\]

\[
\delta Q_n = \int d\mathbf{r} (\nabla \delta \rho_n(\mathbf{r})).
\]

In the case of dipolar operator \( \hat{q} = z (l = 1) \) we find

\[
\delta Q_n = Z_n \rho_n(\mathbf{r}) \int d\mathbf{r} \rho_m(\mathbf{r}) \left( \frac{\delta^2}{\delta \rho} \rho_n(\mathbf{r}) \right).
\]

Note that these results are consistent with the picture of coupling by moments of the dynamic structure factor \( m_3 \) and \( m_1 \) and also with the \( ph, p'h' \) formula for \( \lambda_{ph,p'h'} \).

2.4. Description of collective excitations

Beyond the numerical simplicity of \( N \)-BSRPA formalism, its power relies on the fact that it gives a lot of access to the physical picture behind various normal modes in a fermionic system. This happens due to the mapping between blocks
\[\gamma_n \rightarrow \pi_n \] and their single particle images. Such physical insight can be used to answer questions regarding the nature of some specific resonances. For that, a good example is provided by C_{60} fullerene where has been a long debate [19–22] about whether the 40 eV resonance is a surface or a volume plasmon. Also, in our previous work [1], we have used this formalism to prove the collective nature of the Pigmy Dipole Resonance in neutron excess nuclei.

Whether a specific normal mode is a collective mode or not, it can be seen from the simplified picture of degeneracy. In that case, all solutions with \( E = \varepsilon \) correspond to single \( ph \) excitation and exhibits 0% from the total sum rule, while any other resonance is collective by construction.

The specific nature of a collective mode is usually found investigating which subsystems of particles or which spatial domain is excited in that normal mode. From this perspective, the \( N \)-block configuration is suitable, since one can compute the explicit time-dependent expectation value for the transition operator projected on the space \( \gamma_n \) using the equations (3), (5):

\[
\hat{Q}_n^{(k)}(t) = 2|\bar{\Xi}_n^{(k)}|^2 \cos(\omega_k t + \theta_n^{(k)})
\]

\[
\Im \theta_n^{(k)} = \frac{\Im k(\Xi_n^{(k)})}{\Re(\Xi_n^{(k)})}
\]

Where, \( \Xi_n^{(k)} \) is the \( n \)th element of the vector \( \Xi \) corresponding to \( E^{(k)} \) energy, while \( \omega_k \equiv E^{(k)}/\hbar \). The amplitude \( |\Xi_n^{(k)}|^2 \) shows to which extent the subsystem \( \gamma_n \) is active in the \( k \)th resonance. Further \( \theta_n^{(k)} \) has the physical meaning of phase of motion for the observable. This can indicate the relative motion of two image blocks \( \gamma_n \) and \( \gamma_m \). This idea shall be tested in section 3.2 computing the phases \( \theta_n^{(k)} \) for the associated blocks.

2.5. Particular cases

\( N = 1 \) implies a single coupling constant \( \lambda \) which in turn, gives us the original schematic model with separable interaction [3]. The well known associated dispersion relation can be recovered from equation (10) as equation (20), while the strengths of the response function have zero amplitude for \( E = \varepsilon_1 \) and the rest of the solutions make up the total sum rule.

\[
\frac{1}{\lambda} = \sum_i \frac{2|Q_i|^2\varepsilon_i}{E^2 - \varepsilon_i^2}.
\]

Doing so in our formalism, we can construct a \( N - BSTDA \) (N-block separable Tamm-Dancoff approximation) with a set of equations identical with system (12), but in which the definition for the \( \hat{\chi}(E) \) matrix elements is \( \hat{\chi}_n = \sum_{\varepsilon_{1,2}}|Q_i|^2/(E - \varepsilon_i) \).

The degenerate limit before mentioned is customary in nuclear physics for rough, schematic calculations. It correspond to setting \( \varepsilon_i \equiv \varepsilon, \forall i \in \pi \) and it is motivated by the empiric form of the self consistent ground state nuclear potential which can be approximated with that of a harmonic oscillator. The same picture is valid in the empirical shell model in cluster physics. Using this in the system of equations (9), we obtain a simple eigenvalue problem:

\[
|Q|^2 \hat{\Xi} = \frac{E^2 - \varepsilon^2}{2\varepsilon} \Xi.
\]

It follows that the solutions of the dispersion relation can be written as \( E^{(k)} = \pm \sqrt{\varepsilon^2 + 2\varepsilon z_k} \), where \( \{z_k\} \) are the eigenvalues of the \( |Q|^2 \hat{\Xi} \) matrix with the normalization condition \( \Xi^\dagger |Q|^2 \hat{\Xi} = \varepsilon/E^{(k)} \). At this end, we recognize that in our previous work we have not linked the analytical solutions derived in there and the fact that they were eigenvalues of a certain matrix \( (|Q|^2 \hat{\Xi}) \).

\( N = 2 \) & degeneracy. Combining these two cases we arrive at the trivial formula for the collective energy as \( E^2 = \varepsilon^2 + 2\varepsilon z_1 \). Since the TKR sum rule states \( m_1 = 2|Q|^2 \) we have \( E^2 = \varepsilon^2 + 2m_1 \varepsilon \). This gives us a first insight into the magnitude of the coupling constant. For the surface plasmon in a sodium cluster we have \( E \approx 3 \) eV, \( \varepsilon \approx 1 \) eV and \( m_1 = Z\hbar^2/2m \), thus \( \lambda \approx 16.82 \) eV/m².

Finally, we should link the generalized static polarizability for the \( \hat{\tilde{q}} \) operator with solutions provided by our formalism since it will serve as a supplementary test of the method:

\[
\alpha(Q) = \sum_k \frac{\Xi_n^{(k)}|^2}{E_k},
\]

3. Results and discussion

Before investigating the dipolar response in some metal clusters and \( C_{60} \) fullerene by means of the present formalism, it is important to give a short description on the numerical details of the ground state calculations.

It is known [6] that the response of clusters to external perturbations in the linear regimes is dictated by the valence electrons, while the core electrons and the nuclei remain frozen. For that, the atomic background can be modelled as a positive charge distribution called 'jellium':

\[
\rho_{jel}(r) = \rho_0[1 + \exp(\sigma(|r| - R_{jel}))]^{-1},
\]
where
\[
R_{\text{jel}} = r_0 \left( 1 + \sum_{lm} \alpha_{lm} Y_{lm} (\Omega) \right).
\]

\( \rho_{0} \) is equal to the ratio \( 3/4\pi r_{s}^{3} \), where \( r_{s} \) is the Wigner-Seitz radius. In practice, this value is adjusted such that \( \rho_{\text{jel}} \) obeys the normalization condition \( \int d^{3}r \rho_{\text{jel}}(\mathbf{r}) = Z \), where \( Z \) is the number of atoms in cluster. The parameters \( r_0 = rZ^{1/3} \) and \( \alpha_{lm} = \alpha_{lm}^{\text{diff}} \) are a measure of the deformation of the cluster and \( \sigma \) accounts for the diffusive character of the jellium which is known to give better results than the step profile \( (\sigma \to \infty) \).

The ground state of the system was obtained by solving the DFT-LDA equations
\[
\hat{h} \phi_{j} (\mathbf{r}) = \varepsilon_{j} \phi_{j} (\mathbf{r}),
\]
\[
\hat{v}_{\text{KS}} (\mathbf{r}) = \hat{v}_{\text{ion}} (\mathbf{r}) + \hat{v}_{H} (\mathbf{r}) + \hat{v}_{\text{xc}} (\mathbf{r}).
\]

\( \hat{v}_{\text{ion}} \) is the potential created by the ionic background, the Hartree potential \( \hat{v}_{H} \) is subject to Poisson equation \( \nabla^{2} \hat{v}_{H} = -4\pi \rho (\mathbf{r}) \) and the exchange-correlation potential \( \hat{v}_{\text{xc}} \) is approximated with the Gunnarson-Lundqvist functional [34]:
\[
\hat{v}_{\text{xc}} [\rho] = -\left( \frac{3\rho}{\pi} \right)^{1/3} - 0.0333 \ln \left( 1 + 11.4 \left( \frac{4\pi \rho}{3} \right)^{1/3} \right).
\]

The residual two-body interaction prescribed by (25) can be written explicitly as:
\[
\frac{\delta \hat{h}}{\delta \rho}(\mathbf{r}, \mathbf{r}') = \frac{e^{2}}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta \hat{v}_{\text{xc}} (\mathbf{r})}{\delta \rho (\mathbf{r}')} \delta (\mathbf{r} - \mathbf{r}').
\]

Now, the numerical difficulty posed by RPA is obvious, being reflected in the \( A_{ph,p'h'} \) terms which are computed as 6D integrals of the Coulomb kernel. The LDA nature of the exchange-correlation potential simplifies the evaluation of the corresponding part of the matrix elements to 3D integrals.

Numerically, we solved the eigenvalue problems (25) for general clusters using a code that discretizes the equations on a 3D uniform grid with a step of \( \approx 0.1r_{0} \) for a box with a length \( \approx 4.8r_{0} \). The eigenvalue problem is solved using the imaginary time method coupled with the split-operator technique. The kinetic operator has been represented in the Fourier space, as well as the Coulomb potential. For simplicity, we consider the jellium representation, ignoring the ionic configuration. More computational details on the DFT-LDA method for clusters can be found in [7, 35].

The DFT-LDA code was extended in two directions: NBSRPA and RPA (for comparison). The RPA routines deal with 3 main points: computing the \( \{ Q_{ph} \}, \{ \varepsilon_{ph} \}, \{ A_{ph,p'h'} \}, \{ B_{ph,p'h'} \} \) terms, solving the RPA eigenvalue problem (6) and constructing the spectrum.

The NBSRPA routines solve the following tasks:
   i. Compute \( \{ Q_{ph} \}, \{ \varepsilon_{ph} \} \);
   ii. Define the blocks by choosing \( \{ \gamma_{\alpha} \} \);
   iii. Compute \( \{ \lambda_{mm} \} \) from equations (16) for each block pair;
   iv. Construct the \( \gamma_{\alpha} (E) \) functions;
   v. Solve the dispersion relation equation (10);
   vi. Solve the system of equation (9);
   vii. Normalize the solutions as in (12);
   viii. Construct the spectrum (13);

The first point, (i), also implemented by RPA, requires just moderate computational resources, since it computes one-body integrals \( (Q_{ph}) \) and scales as \( O(\text{occ} \times \text{unocc}) \). The second point, (ii), is even easier to implement, scaling as \( O(\text{occ}) \). The computational complexity for the (vi), (vii), (viii) tasks scales as \( O(N^{3}), O(N), O(\text{occ} \times \text{unocc}) \), but the required CPU time is negligible.

The most expensive computational parts of NBSRPA are the (iii) and (v) points. The former requires similar calculations as the \( A_{ph,p'h'} \) terms, but while in RPA we have an \( O(\text{occ}^{2} \times \text{unocc}^{2}) \) scaling, in the present approach the scaling is only \( O(N^{2}) \). At this level, our method is computational superior to standard RPA. The later point, (v), deals with finding the real roots of a polynomial of order \( 2\text{occ} \times \text{unocc} \) in \( E \). While the solutions lie in an \( a \text{ priori} \) known interval (from experiment), their computation must be performed with good relative accuracy (\( 10^{-5}\% \) convergence) in order to obtain later (point vii) the correct normalization of the vectors \( \Xi \).

### 3.1. Sodium clusters

For sodium clusters we use \( r_{c} \approx 3.93 \) a.u. for the calculation of \( r_0 \) while the diffusive part of the jellium model is taken \( \sigma \approx 1 \) a.u.\(^{-1}\). The spherical shaped clusters \( N_{4}^{(1)} \) (with a magic number: \( Z = 2, 8, 20, 40, 58, 92, 138 \ldots \) of atoms) are easier to tackle numerically, both from the perspective of DFT-LDA as well as of RPA calculations (for details, see [36]) given the spherical symmetry. Consequently, the ground state eigenvalues of the Hamiltonian operator have a high level of degeneracy in terms of angular momenta quantization. Their optical spectra exhibits a strong surface plasmon around 2.5–3 eV. For deformed cluster we use the parametrization (24) with the deformation parameters taken as in [37].
In such deformed clusters, the giant surface plasmon is split in two or more peaks, phenomenon known as Landau fragmentation [38]. From the numerical perspective, solving the KS equation demands the discretization in a cylindrical or the in full 3D cartesian system of coordinates. This removes the angular degeneracy associated with the spherical symmetry and the dimension of the RPA problem is considerably enlarged. Moreover, the \( ph, p' h \) matrix elements require more computation effort.

As a demonstration of the numerical results regarding the DFT-LDA ground state, we plot in figure 1 the radial profile of the electronic density in \( Na_{40} \) and the first few energetic levels in the KS potential.

From the LDA solutions, the computation of \( ph \) excitation energies and the corresponding matrix elements \( Q_{ph} \) is straightforward. The present developed formalism is general and valid for any transition operator \( \hat{q} \) as long as the block-separable ansatz holds. In practice we are interested in the optical response which is connected with the dipolar operator \( \hat{q} = z \). More complex local operators of the following form: \( q(r) = r^{p}Y_{lm}(\Omega) \) [39] can be used to describe surface plasmons of various multipolarities. To account for the volume plasmons one should employ operators which have non-zero laplacian character, generically \( q(r) = r^{p}Y_{lm}(\Omega), p \neq 1 \).

Regarding the dipolar operator, we plot the single particle strengths \( |Q_{ph}|^2 \) versus the excitation energies \( \varepsilon_{ph} \) in figure 2 for the spherical \( Na_{58} \) cluster. As one can see, a large fraction of the sum rule is collected around the \( \varepsilon \approx 0.9-1 \) eV, fact which justifies as a zero-th approximation the degenerate limit. In particular, we compute this quantity as:

\[
\varepsilon = \frac{\sum_{\phi \rho} \varepsilon_{\phi \rho} |Q_{\phi \rho}|^2}{\sum_{\phi \rho} |Q_{\phi \rho}|^2} = \frac{m_1(Q)}{m_0(Q)}
\]

1—BSRPA & degeneracy. As discussed in section 2.5, the collective resonance energy prescribed by this case it is given by \( E^2 = \varepsilon^2 + \frac{3h^2\varepsilon^2}{4\pi m r^3} \), a result which makes the resonance energy \( \varepsilon \) dependent. Disregarding the sphere model and doing realistic calculations for the coupling constant with the ground state LDA density and degenerate excitation energy we obtained a set of values which are shown in figure 3 (blue dots) for various neutral sodium clusters. These results are in good agreement with the experimental values for the surface plasmon in neutral clusters \( 2.5 \text{eV} < E < 3 \text{eV} \). Moreover, we can observe the asymptotic trend towards the maximal Mie value for very large clusters.

2—BSRPA & degeneracy. We define two block images \( \gamma_{1}, \gamma_{2} \) with respect to the mean squared radius of the orbitals as it follows \( \gamma_{1} : \langle r^2 \rangle < 0.6 \rho_{0}^2 \) and \( \gamma_{2} : \langle r^2 \rangle > 0.6 \rho_{0}^2 \). The interpretation would be that the first image describes the volume of the cluster, while the second, the surface. Solving the eigenvalue problem (21) we find two energies \( E_{1} \) and \( E_{2} \) show in figure 3. The first is very close to the results for \( N = 1 \) and exhibits around 90% of the total sum rule while the latter \( 1.4 \text{eV} \) is unphysical giving around 10% of the sum rule but not being present in experimental optical spectra. Regarding their specific interpretation, we compute at \( \varepsilon_{\gamma_{1}}(k) \), \( \varepsilon_{\gamma_{2}}(k) \) for each block image and we obtain \( \varepsilon_{\gamma_{1}}(1) \approx 6\% \), \( \gamma_{1}(1) = +\pi \), \( \varepsilon_{\gamma_{2}}(1) \approx 4\% \), \( \gamma_{2}(1) = -\pi \), \( \varepsilon_{\gamma_{2}}(2) \approx 9\% \), \( \gamma_{2}(2) = +\pi \) and \( \varepsilon_{\gamma_{2}}(2) \approx 91\% \), \( \gamma_{2}(2) = +\pi \). This tells us that the unphysical resonance is described by almost equal amplitude out-of-phase oscillations of the volume and the surface of the electron cloud while the large energy resonance is described by in-phase oscillations with a small amplitude for the volume image and a large amplitude for the surface image. Thus, we have obtained by means of our formalism the correct values and interpretation for the surface plasmon observed in sodium clusters.

1—BSRPA & full \( ph \) data. We take again the dispersion equation (20) and solve it using realistic \( ph \) excitation energies (not the degenerate limit) together with their \( Q_{ph} \). We did this for a series of singly charged sodium clusters, but we plot in figure 4 the results for \( Na_{7} \) (which is deformed) and \( Na_{7} \) (spheroidal). We compare the obtained spectra with the RPA

![Figure 2. Single particle \( ph \) excitation strengths in \( Na_{58} \) for the dipole operator](image)

![Figure 3. 1—BSRPA resonance (blue) and 2—BSRPA resonances (red and black) in the degenerate limit of various sodium clusters vs the inverse of the radius.](image)
results (red, dashed). We find fairly good agreement in the position of the surface plasmon, but, as in the degenerate 2-BSRPA case, a peculiar resonance appears at about 1.5 eV. We explain this result from the poor representation of the two-body interaction by means of a single coupling constant. The same explanation we assert to the lack of Landau fragmentation of the surface plasmon for the deformed cases, as $Na_{41}^+$. Exploring extensively further cases, we have found that the formalism of 4-BSRPA when the single particle image of the blocks is predefined after the square radius value $r^2$ offers the best computational-accuracy ratio. In this respect we have performed systematic calculations for singly charged sodium clusters of various deformations in between $Na_{15}^+$ and $Na_{58}^+$. The results can be seen in figure 5 where the full-RPA results are also presented for a few clusters. These results can be compared with experimental spectra from [40, 41].

As a supplementary test, we compare the static polarizabilities obtained with our method (equation (21)) and the experimental ones [42] in figure 6.

After spanning all these results, we conclude that our formalism is able to offer a pertinent description of the optical spectra and static polarizabilities in sodium clusters obeying the TKR sum rule when the case of $N = 4$ blocks is considered. From the numerical perspective, our results have been obtain roughly by an order of magnitude faster in terms of CPU time than the ones obtained with RPA.

### 3.2. C$_{60}$ Fullerene

Since the discovery of C$_{60}$ fullerene [43] a lot of experimental and theoretical attention has been drawn towards its
spectacular properties. In particular, its optical spectrum is known to be dominated by two surface plasmons around 20 eV and 40 eV [24, 44–46]. In electron energy loss experiments three volumes plasmons emerge in the 20–30 eV range [47]. The theoretical work done in this direction has been able to reproduce the experimental values from many perspectives as RPA [48], TDDFT [24], time-dependent Thomas Fermi [49], etc.

In order to solve the KS equations for the ground state we have modelled the ionic background accordingly with [24, 44] defining a jellium shell \( \rho_{\text{jel}}(r) \propto \Theta(r-r_1) \Theta(r_2-r) \) centred on the position of the carbon nuclei, where \( r_1 = 2.8 \, \text{Å}, \ r_2 = 4.2 \, \text{Å} \) and normalized to \( n = 240 \) which is the number of considered valence electrons. Following [50] we have added a supplementary pseudopotential \( V_0 \) to the total KS potential in order to account for the ionic structure. Due to the spherical symmetry of the cluster of \( C_{60} \) we were able to solve numerically only the radial KS problem. For the calculation of matrix elements we have used the spherical multipolar expansion of the Coulomb kernel (for more details about calculations of RPA in spherical systems see [36]). In figure 8 is plotted the ground state electron density, the effective KS potential and the first few energetic levels. Further we shall investigate the dipolar response of \( C_{60} \) following the same path as for sodium clusters.

1–BSRPA & degeneracy. The dispersion relation for the collective resonance described by this case can be written \( E^2 = \varepsilon^2 + Z e^2 / m \). Using the degenerate energy \( \varepsilon \approx 10 \, \text{eV} \) and modelling the total density of electrons as a shell of charge identical with the jellium we find \( E \approx 16.7 \, \text{eV} \) while doing realistic calculations of \( \lambda \) from the ground state density, we find \( E \approx 18 \, \text{eV} \).

3–BSRPA & degeneracy. Having the geometrical structure of \( C_{60} \) as a spherical shell, we define three block images \( \gamma_1, \gamma_2, \gamma_3 \) with some empirical image densities \( \rho_1, \rho_2, \rho_3 \) of spherical gaussian shape, such that the total ground state density of electrons is fairly reproduced. By this definition, \( \gamma_1 \) is centred at about \( 0.9 r_0 \), \( \gamma_2 \) at \( r_0 \) and \( \gamma_3 \) at \( 1.1 r_0 \), thus the images represent the inner surface, the volume and the outer surface of the cluster. We compute the associated coupling strengths and solve the eigenvalue problem in the degenerate case finding quite robust solutions with respect to the parameters of gaussians.

The results are presented in table 1 for energies and associated strengths and phases. We find that the small energy resonance exhibits around 8% of the total sum rule being described by a collective dipole oscillation in phase of all subsystems. The large resonance from \( E_2 \) is consistent with the standard interpretation of in-phase oscillation of the surfaces while the volume of the cluster remains quite inert. Regarding the largest energy, this can be interpreted from the strengths and phases as an out-of-phase surface variation of the density. This picture of two oscillating surfaces out of phase but no significant volume oscillation is consistent with the interpretation obtained in other models [20, 45, 46, 49].

We have explored further limits of the formalism and have found that the case 5–BSRPA with the blocks images defined after their mean squared radius provides the best results with minimum of effort. The resulting spectrum vs experimental results can be seen in figure 8. As a final test we compute the static polarizability and we obtained \( \alpha \approx 93 \, \text{Å}^2 \) compared with the experimental \( \alpha = 76.5 \pm 8 \, \text{Å}^2 \) [51].

The overall numerical complexity of the method scales roughly like \( c + O(N^s) \) (with \( s \approx 2 - 2.5 \)) where \( c \) is a constants related to some inherent calculations which are independent of \( N \). On the other hand, the numerical precision (computed as \( L_2 \) norm of the relative error in respect with the RPA spectrum) scales as \( O(N^{-1}) \). Therefore, the product between error and numerical costs is minimized when \( N \sim \sqrt{c} \). From this perspective it can be understood the
existence of an optimal number of blocks \( N \) of the method (5 for \( C_{60} \) and 4 for sodium clusters).

Conclusions

Starting from DFT derived RPA equations for a system of fermions we employ the ansatz of separable residual interaction defining \( N \) blocks of \( ph \) excitation with specific coupling constants between them. We show that, in the frame of this approximation, the RPA eigenvalue problem can be converted in a homogeneous system of \( N \) equations. The associated dispersion equation and the normalization condition are derived for the unknowns of the reformulated problem. Following some prescription for the definition of the blocks, we find an approximative way of computing the coupling constants.

The present \( N \)-BSRPA formalism offers a powerful alternative to the standard RPA equations due to highly reduced numerical effort needed. In turn, the results are in good agreement with experimental or RPA calculations for the dipolar modes, as it was tested, at least for sodium clusters or \( C_{60} \) fullerene. Moreover, the formalism gives us access to the interpretation of various collective modes investigating specific quantities as the vector solutions of the system and the associated phases of motion. In this respect we have confirmed once again that the correct interpretation for the near 40 eV resonance present in the spectrum of \( C_{60} \) fullerene is a surface plasmon made up by the out-of-phase oscillations of the inner and outer surfaces of the electron cloud.

We conclude that the \( N \)–BSRPA is a valid alternative to the high costs of the full RPA calculations and we support the idea that the present formalism could find applications in many other systems from nuclear to solid state physics, and that it could be extended as to include other physical phenomena (e.g. pairing).

Acknowledgments

For this work V Baran was supported by a grant of the Romanian National Authority for Scientific Research, CNCS—UEFISCDI, project number PN-II-IDPCE-2011-3-0972.

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