EXTENSION OF THE THOMAS-REICHE-KUHN SUM RULE TO A SCHIFF-LIKE DIPOLE MOMENT

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The Thomas-Reiche-Kuhn sum rule is corrected due to the specific structure of the Schiff-like dipole moment. The corrections are evaluated alternatively within the RPA approach and by using a series expansion for the charge density around the value corresponding to the jellium sphere. The latter procedure provides a nonlinear $\mathcal{N}$ dependence for the new sum rule, where $\mathcal{N}$ represents the number of cluster components. The new sum rule is satisfactorily obeyed by the RPA procedure and quite well when the density expansion is used.

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I. INTRODUCTION

The Thomas-Reiche-Kuhn (TRK) sum rule [1–3] was discovered around the date of quantum mechanics founding. This sum rule has been widely applied to the problems of electron excitations in atoms, molecules, and solids due to its direct relation to the photoabsorbtion oscillator strength [4–7].

The many body properties like collective excitations in atoms, molecules or clusters are studied using different collective models. Thus, the random phase approximation (RPA) formalism has been extensively used and excellent results for the photoabsorbtion cross section spectra, especially in the atomic clusters domain [8–10] were obtained.

In a previous publication [10], some of the many body features of the small and medium sodium clusters were studied within the RPA approach using a projected spherical single-particle basis. In the quoted work, the RPA wave functions were used to treat the dipole transitions which led to the photoabsorbtion cross section spectra. Also, expressions for the system static electric polarizability were analytically derived. The numerical results for *Na* clusters are in a very good agreement with the experimental data. The correspondence of the RPA results to the photoabsorbtion cross section is strictly related to the fact that the RPA preserves the

energy-weighted TRK sum rule. This is however true if the transition operator is simply the electric dipole moment, which is not the case in the above quoted paper where, indeed, a modified dipole operator (similar with Schiff-like dipole moment [11–14]) is used. In this situation a natural question arise: what happens to the sum rule?

The goal of the present work is to answer to this question. This is done by comparing the result of direct energy-weighted summation of the reduced dipole transition probabilities with an analytical expression of this sum derived for the Schiff-like dipole moment operator. The corrections to the matrix elements corresponding to the standard expression of the dipole moment are, in general, not small and therefore sizable changes in the usual TRK sum rule are expected. Hence, it seems to be very important to associate a new sum rule to the newly defined dipole operator.

For this purpose, in the following sections two different approaches for determining the sum rule corrections are presented. One method uses the results of the RPA equations, such as the phonon amplitudes corresponding to the chosen particle-hole basis, to determine the correction to the original TRK sum rule. Another approach is based on a specific assumption for the electron density shape, given by its dependence on the radial coordinate, which were proved [10] to be quite realistic in describing the static electric polarizability of the cluster.

The paper is structured as follows. In Sec. II, we briefly review the RPA results obtained in a previous work and define the sum rule corresponding to the newly adopted dipole moment. Two model calculations for the energy-weighted sum of the transition probabilities, are presented in Sections II and III, respectively. The difference between the two methods consists in the ways the average values of the r^2 and r^4 operators with the system ground state, are evaluated. Section V is devoted to the numerical results of the modified sum rule obtained by using the mentioned methods. The final conclusions are summarized in Sec. VI.

II. THE RPA DIPOLE SUM RULE

Within the RPA formalism, for any Hermitian operator $\hat{M}$, the following sum rule holds

$$\sum_n (E_n - E_0)\left|\left\langle 0\left|\hat{M}\right|1_n\right\rangle\right|^2 = \frac{1}{2}\left\langle 0\left|\left[\left[\hat{M},H\right],\hat{M}\right]\right|0\right\rangle, \tag{2.1}$$

where E_n are the RPA energies corresponding to the n-th order solution of the RPA equations associated to the many body Hamiltonian H. Here the state $|0\rangle$ is the RPA phonon vacuum, while $|1_n\rangle$ denotes the single phonon state defined by

$$|1_n\rangle = C_n^\dagger |0\rangle, \tag{2.2}$$

with $C_n^\dagger$ being the phonon creation operator. We are interested in those features of atomic clusters which are determined by the valence electrons. The valence electrons are supposed to move in the mean field of the ionic core and interact among themselves through a Coulomb force. In the local density approximation [16, 17], the residual two-body interaction can be expanded in multipole series from which only the dipole term is relevant and therefore considered. Treating the one-body term represented by the mean field together with the dipole term of the two-body interaction within the RPA formalism [10], leads to the definition of the phonon operator for this particular case of atomic clusters:

$$C_n^\dagger(1,\mu) = \sum_{ph}\left[X_{ph}^n\left(c_p^\dagger c_h\right)_{1\mu} - Y_{ph}^n\left(c_h^\dagger c_p\right)_{1\mu}\right], \tag{2.3}$$

which is subjected to the conditions

$$\left[H, C_n^\dagger\right] = E_n C_n^\dagger, \tag{2.4}$$

$$\left[C_n, C_{n'}^\dagger\right] = \delta_{nn'}. \tag{2.5}$$

Here X_{ph}^n and Y_{ph}^n are the RPA forward-going and backward-going amplitudes corresponding to the *n*-th order solution of the RPA equations. Solving the RPA equations [18] one determines the phonon energies and amplitudes.

The reduced probability for the dipole transition $|0\rangle \to |1_n^+\rangle$ can be written in terms of the RPA phonon amplitudes and the *ph* matrix elements of the transition operator[1]:

$$B\left(E1, 0^+ \to 1_n^+\right) = \left|\langle 0\|\mathcal{M}(E1)\|1_n^+\rangle\right|^2, \tag{2.6}$$

where

$$\langle 0\|\mathcal{M}(E1)\|1_n^+\rangle = \sum_{ph}\hat{I}_p\langle p\|\mathcal{M}(E1)\|h\rangle\left[X_{ph}^n + (-)^{I_p+I_h}Y_{ph}^n\right] \tag{2.7}$$

are the reduced matrix elements of the dipole operator $\mathcal{M}(E1)$, between the specified RPA states.

As we already mentioned, instead of the usual transition dipole operator a Schiff-like moment operator [11–14] was used.

$$\mathcal{M}(E1) = e\left(1 - \frac{3}{5}\frac{r^2}{r_s^2}\right)\vec{r}. \tag{2.8}$$

Here r_s is the Wigner-Seitz radius and have the value of 3.93 a.u. for *Na* clusters. The corrective component, involved in the dipole operator, relates particle and hole

[1] Throughout this paper the Rose's convention for the reduced matrix elements are used.

states characterized by $\Delta N = 3$, which results in modifying the strength distribution among the RPA states. Such an effect is obtained in a natural manner, i.e. using the standard form for the dipole transition operator, if the mean field potential for the single particle motion involves higher powers of the radial coordinate.

The dipole moment operator (2.8) satisfies the sum rule given by Eq. (2.1). In order to connect the sum rule with the RPA transition probabilities (2.6) it is necessary to use the reduced matrix elements in Eq. (2.1). The new form for the sum rule expression reads:

$$\sum_n (E_n - E_0)\left|\langle 0\|\mathcal{M}(E1)\|1_n\rangle\right|^2 = \frac{3}{2}\langle 0|\left[\left[\mathcal{M}(E1),H\right],\mathcal{M}(E1)\right]|0\rangle. \tag{2.9}$$

The double commutator involved in the right hand side can be analytically calculated. Aiming at this goal we suppose that the many body Hamiltonian of N particles (electrons) has the form

$$\hat{H} = \sum_{\alpha=1}^{\mathcal{N}} \frac{p_\alpha^2}{2m_e} + \sum_{\alpha\neq\beta}^{\mathcal{N}} V_{\alpha\beta}(\vec{r}), \tag{2.10}$$

where the first term is the kinetic energy and the last one is the interaction potential between the system components. Since the potential term depends only on space coordinate, it will commute with the dipole operator, and the right hand side of the sum rule (2.9) will be completely determined by the double commutator of the kinetic energy and the dipole operator.

$$\left[\left[\mathcal{M}(E1),H\right],\mathcal{M}(E1)\right] = \sum_{\alpha=1}^{\mathcal{N}}\left[\left[\mathcal{M}(E1),\frac{p_\alpha^2}{2m_e}\right],\mathcal{M}(E1)\right] \tag{2.11}$$

According to the details given in Appendix A, the final result for this double commutator is:

$$\begin{aligned}\sum_n (E_n - E_0)\left|\langle 0\|\mathcal{M}(E1)\|1_n\rangle\right|^2 = \frac{9\hbar^2 e^2}{2m_e}\Bigg[\mathcal{N} - \frac{2}{r_s^2}\langle 0|\left|\sum_{\alpha=1}^{\mathcal{N}} r_\alpha^2\right||0\rangle + \\ + \frac{33}{25 r_s^4}\langle 0|\left|\sum_{\alpha=1}^{\mathcal{N}} r_\alpha^4\right||0\rangle\Bigg].\end{aligned} \tag{2.12}$$

One may check that the same result is obtained if the generalized TRK sum rule is used [15]:

$$\sum_n (E_n - E_0)\left|\langle 0\|\vec{F}(\vec{r})\|1_n\rangle\right|^2 = \frac{3\hbar^2}{2m_e}\sum_{i=x,y,z}\langle 0|\left(\vec{\nabla}F_i\right)\cdot\left(\vec{\nabla}F_i^\dagger\right)|0\rangle. \tag{2.13}$$

which is satisfied for any vector operator $\vec{F}(\vec{r})$ depending exclusively on the vector radius $\vec{r}$.

Some comments on the formula (2.12) are necessary. First of all, if the adopted Schiff-like dipole moment is restricted to the normal dipole operator, *i.e.* the correction term is omitted, then the right hand side of the above formula is reduced to the first term. This result is just the TRK sum rule for the simple dipole moment. The terms correcting the standard TRK sum rule are in fact expected values of the radius powers r^2 and r^4, in the RPA ground state. Obviously, these corrective terms induce an additional $\mathcal{N}$ dependence for the energy weighted sum rule. As for the left hand side of Eq. (2.12), this can be directly calculated using the RPA output data, like energies and transition probabilities which, as a matter of fact, were found in our previous publication [10].

In the next two sections two different approaches for determination of the mean values of powers of the radial coordinate on the RPA vacuum states are presented. The results of these models are to be compared with the directly calculated sums. Satisfying the equation (2.12) by a model calculation is a powerful test for the theoretical assumptions. The terms involved in the left hand side contribute by different amount to the total sum. If the summation involves a collective state, this saturates the sum rule to a large percentage. If the collectivity is fragmented among several states then these states bring the major part of the total transition strength. In the situation when the strength is distributed among many states, the saturation of the sum rule is achieved only by increasing the dimension of the *ph* excitations considered in the RPA treatment.

III. THE RPA APPROACH

The correction terms from the right hand side of the equation (2.12), which will be here-after denoted as $\mathcal{S}(\mathcal{N})$, can be expressed in terms of particle-particle (*pp*) and hole-hole (*hh*) transition components. Indeed the *ph* transition components give vanishing contributions when they are averaged with the RPA ground state. Therefore the one-body operator $\hat{r}^m$ can be written in the second quantization as:

$$\sum_{\alpha=1}^{\mathcal{N}} r_\alpha^m \equiv \sum_p \langle p | r^m | p \rangle c_p^\dagger c_p + \sum_h \langle h | r^m | h \rangle c_h^\dagger c_h. \tag{3.1}$$

Now we wish to express the fermion density operators $c_p^\dagger c_p$ and $c_h^\dagger c_h$, in terms of the RPA phonon operators $C_n^\dagger (C_n)$. This task can be achieved by supposing the following representations for the operator pairs $c_p^\dagger c_p$ and $c_h^\dagger c_h$ respectively:

$$c_p^\dagger c_p = \sum_n \alpha_n^p C_n C_n^\dagger, \tag{3.2}$$

$$c_h^\dagger c_h = \sum_n b_n^h C_n C_n^\dagger. \tag{3.3}$$

The coeffcients a_n^p and b_n^h can be determined from the following commutation relations:

$$\begin{aligned} a_n^p &= \langle 0 | \left[\left[C_n^\dagger, c_p^\dagger c_p \right], C_n \right] | 0 \rangle, \\ b_n^h &= \langle 0 | \left[\left[C_n^\dagger, c_h^\dagger c_h \right], C_n \right] | 0 \rangle. \end{aligned} \tag{3.4}$$

By simple algebraic manipulations we easily arrive at the final expressions for the coeffcients a_n^p and b_n^h.

$$\begin{aligned} a_n^p &= \sum_h \left(X_{ph}^{(n)^2} + Y_{ph}^{(n)^2} \right), \\ b_n^h &= -\sum_p \left(X_{ph}^{(n)^2} + Y_{ph}^{(n)^2} \right). \end{aligned} \tag{3.5}$$

In this way the operators $c_p^\dagger c_p$ and $c_h^\dagger c_h$ can be written as follows

$$\begin{aligned} c_p^\dagger c_p &= \sum_n \sum_h \left(X_{ph}^{(n)^2} + Y_{ph}^{(n)^2} \right) C_n^\dagger C_n, \\ c_h^\dagger c_h &= -\sum_n \sum_h \left(X_{ph}^{(n)^2} + Y_{ph}^{(n)^2} \right) C_n^\dagger C_n. \end{aligned} \tag{3.6}$$

Using these phonon representations together with the orthogonality property of the RPA one phonon states,

$$\langle 0 | C_n C_{n'}^\dagger | 0 \rangle = \delta_{nn'}, \tag{3.7}$$

the following expression for the average of the power operator r^m on the RPA vacuum states, is obtained:

$$\langle 0 \| r^m \| 0 \rangle = \sum_n \sum_{ph} \left(X_{ph}^{(n)^2} + Y_{ph}^{(n)^2} \right) \left(\langle p | r^m | p \rangle - \langle h | r^m | h \rangle \right). \tag{3.8}$$

A specific ingredient of our formalism is the projected spherical single particle basis which is used by the RPA formalism [10]:

$$\begin{aligned} &\phi_{IM;\sigma}(nl;d) = \mathcal{N}_{nl}^I(d) \left[P_{MI}^I | nlI \rangle \Psi_c(d) \right] \mathcal{X}_\sigma, \text{ for } I \neq 0, l = even, \\ &\phi_{00;\sigma}(nl;d) = \mathcal{N}_{nl}^0(d) \left[P_{00}^0 \left[| nl \rangle \hat{s} \right]_{l+1,0} \Psi_c(d) \right] \mathcal{X}_\sigma, \text{ for } I = 0, l = odd, \end{aligned} \tag{3.9}$$

where $\hat{s}$ denotes the spin operator and $\mathcal{X}_\sigma$ is the bi-spinor component. The standard notation for the angular momentum projection operator was used:

$$P_{MK}^I = \frac{2I+1}{8\pi^2} \int D_{MK}^{I*}(\Omega) \hat{R}(\Omega) d\Omega. \tag{3.10}$$

The norms $\mathcal{N}_{nl}^{I}(d)$ of these projected states are

$$\begin{aligned} \left[\mathcal{N}_{nl}^{I}\right]^{-2} &= \sum_{J}\left(C_{I0I}^{lJI}\right)^{2}\left(N_{j}^{(c)}\right)^{-2}, \text{ for } I \neq 0,\ l = even, \\ \left[\mathcal{N}_{nl}^{0}\right]^{-2} &= \frac{1}{4}\frac{1}{2l+3}\left(N_{l+1}^{(c)}\right)^{-2}, \text{ for } I = 0,\ l = odd, \end{aligned} \tag{3.11}$$

with $N_{J}^{(c)}$ denoting the norm of the J component projected from the deformed state $\left|\Psi_{c}\right\rangle$, describing the core.

The diagonal matrix elements of the operator r^m are expressed only through the radial integrals:

$$\left\langle i\left|r^{m}\right|i\right\rangle = \nu^{2}\left(I_{i}\right)\int_{0}^{\infty}\left[R_{n_i l_i}\left(r\right)\right]^{2} r^{m+2}dr,\ i = p,h, \tag{3.12}$$

where $R_{n_i l_i}(r)$ represents the radial part of the spherical shell model single particle wave functions, with indices n_i and l_i denoting the number of nodes for the corresponding single particle states and the angular momentum of the particles and holes participating in the excitations, respectively. $\nu\left(I_{i}\right) = \dfrac{2-\delta_{I_i,0}}{2I_{i}+1}$ is a statistical factor which reflects the fact that for a given energy level with angular momentum I on each of the $2(2I + 1)$ degenerate states are distributed 4 electrons with a constant probability. If $I = 0$ the number of electrons occupying the state is 2.

IV. ELECTRON DENSITY APPROACH

Static electric polarizabilities results based on the calculations for the number of spilled out electrons [10], agree quite well with experimental data. These spilled out electrons produce a screening effect against external fields which results in changing the classical result for the polarizability. The basic assumption in accounting the spilled out electrons is the fact that the electron density is not going sharply to zero at the cluster surface, but is gradually decreasing and moreover extends significantly beyond the jellium edge. The same argument can be brought for the correction terms of the $\mathcal{S}(\mathcal{N})$ containing averages of the radius powers with the RPA vacuum states. The electronic density has a constant central part, enfolded by a diffuse region for which the electron density tends smoothly to zero. Driven by some parallelism between atomic clusters and nuclear systems [19, 20], the average of r^m with the RPA vacuum states can be expressed in the form of a power series in the variable $\dfrac{a}{R}$:

$$\left\langle r^m \right\rangle = R^m \frac{3}{m+3}\left[1+\frac{\pi^2}{6}\left(\frac{a}{R}\right)^2 m\left(m+5\right)+\ldots\right]. \tag{4.1}$$

Here $R = r_s \mathcal{N}^{1/3}$ is the radius of the cluster with $\mathcal{N}$ atoms, where r_s being the Wigner-Seitz radius, which for the *Na* clusters has the value of 3.93 u.a., and a is a parameter related to the thickness of the diffusion region. In this approximation, the averages of the second and fourth power of radius are

$$\begin{aligned} \left\langle r^2 \right\rangle &= \frac{3}{5}R^2\left[1+\frac{7\pi^2}{3}\left(\frac{a}{R}\right)^2\right], \\ \left\langle r^4 \right\rangle &= \frac{3}{7}R^4\left[1+6\pi^2\left(\frac{a}{R}\right)^2\right]. \end{aligned} \tag{4.2}$$

Using this parametrization, the correction terms of the sum $\mathcal{S}(\mathcal{N})$ acquire a dependency on the cluster's number of atoms:

$$\begin{aligned} \langle 0|\left|\sum_{\alpha}^{\mathcal{N}} r_\alpha^2\right||0\rangle \approx \left\langle r^2 \right\rangle &= \frac{3}{5}r_s^2\mathcal{N}^{2/3}\left[1+\frac{7\pi^2}{3}\left(\frac{a}{r_s}\right)^2\mathcal{N}^{-2/3}\right], \\ \langle 0|\left|\sum_{\alpha}^{\mathcal{N}} r_\alpha^4\right||0\rangle \approx \left\langle r^4 \right\rangle &= \frac{3}{7}r_s^4\mathcal{N}^{4/3}\left[1+6\pi^2\left(\frac{a}{r_s}\right)^2\mathcal{N}^{-2/3}\right]. \end{aligned} \tag{4.3}$$

In this way the sum $\mathcal{S}(\mathcal{N})$ can be written in the following way

$$\mathcal{S}\left(\mathcal{N}\right) = \frac{9\hbar^2 e^2}{2m}\left[\mathcal{N}-\frac{6}{5}\mathcal{N}^{2/3}+\frac{99}{175}\mathcal{N}^{4/3}+\frac{\pi^2 a^2}{5r_s^2}\left(\frac{594}{35}\mathcal{N}^{2/3}-14\right)\right]. \tag{4.4}$$

By inspection, one notices that besides the number of atoms dependency, this expression involves only universal constants, which makes the equation (2.12) to be, indeed, a real sum rule. However, the diffusion parameter is to be determined. Contrary to the nuclear systems, where the thickness of the diffusion region is approximately the same for all nuclei, for atomic clusters the parameter a is expected to have a $\mathcal{N}$ dependency due to the long range character of the two body interaction:

$$\mathcal{S}\left(\mathcal{N}\right) = \frac{9\hbar^2 e^2}{2m_e}\left[\mathcal{N}-\frac{6}{5}\mathcal{N}^{2/3}+\frac{99}{175}\mathcal{N}^{4/3}+\frac{\pi^2 a\left(\mathcal{N}\right)^2}{5r_s^2}\left(\frac{594}{35}\mathcal{N}^{2/3}-14\right)\right]. \tag{4.5}$$

Using the numerical value of the left hand side of the equation (2.12) for the quantity $\mathcal{S}(\mathcal{N})$, the above equation can be used for determining the value of the diffusion parameter a which will assure the exact satisfaction of the sum rule (2.12)

in the framework of this model based on the electron distribution features. An explicit $\mathcal{N}$ dependency of the diffusion parameter can be easily obtained by interpolating the results for a with a function of $\mathcal{N}$. The result is:

$$a(\mathcal{N}) = -0.975157 - 0.0112138\mathcal{N}^{1/3} + 0.360518\mathcal{N}^{2/3} \tag{4.6}$$

Inserting the expression of $a(\mathcal{N})$ (4.6) in Eq. (4.5) one obtains the final sum rule.

V. NUMERICAL RESULTS

The first step is the calculation of the left hand side of equation (2.12), using the results of the RPA calculations from the previous paper [10]. The RPA results, *i.e.* energies and amplitudes depend on the number of atoms in cluster, by means of the oscillator energy quanta $\hbar\omega_0 = E_f(\mathcal{N})/\mathcal{N}^{1/3}$ and the oscillator length $b = \sqrt{\hbar / m_e\omega_0}$. The $\mathcal{N}$ dependency of the Fermi energy is determined by interpolating those values which correspond to the best agreement of the calculated photoabsorbtion curve with experimental points. In general the Fermi energy has a constant value of about 3 *eV* for *Na* clusters, but supposing that it also depends on the number of atoms from the cluster, a Fermi energy varying in the range of 3.3–3.75 *eV*, for the considered region of clusters, was obtained. It is also to be mentioned that the RPA calculations were performed for a restricted space of the particle-hole excitations, including only the $\Delta N = 1$ and $\Delta N = 3$ transitions. Once the RPA amplitudes and energies are determined, using for example the method given in Ref. [18], the electric dipole transition probabilities can be computed by squaring the reduced matrix elements given by Eq. (2.7). The values obtained for the energy-weighted sum of dipole transition probabilities are therefore to be compared with those given by the analytical expressions of $\mathcal{S}(\mathcal{N})$ from the right hand side of the Eq. (2.12). The agreement between these values will prove that the chosen form of the dipole moment satisfies the extended TRK sum rule.

Based on the RPA output data, an analytical expression for the averages of the radius powers with the RPA vacuum states was obtained. In this way the quantity $\mathcal{S}(\mathcal{N})$ can be expressed in terms of the RPA amplitudes X_{ph}^{n} and Y_{ph}^{n} and matrix elements of the operators r^2 and r^4 corresponding to the particle and hole states, respectively (3.9). The dependence on the number of atoms for $\mathcal{S}(\mathcal{N})$ is not obvious since it cannot be explicitly determined. Indeed the RPA results depend on the $\mathcal{N}$ in a very complicated way through the configuration of the particle-hole basis and parameters such as the Fermi energy $E_F(\mathcal{N})$ and oscillator length b. Of course not only the RPA amplitudes hide the $\mathcal{N}$ dependency, but also the matrix

elements on particle and hole states have an indirect relation with the number of atoms in cluster, which is due to the fact that the particle-hole space corresponding to the $\Delta N = 1, 3$ excitations is uniquely determined for each cluster. The numerical results for the $\mathcal{S}(\mathcal{N})$ show in general a monotone behavior in the interval of studied clusters, which is to be expected, because the simple TRK sum rule is proportional with the number of constituents. Obviously, the sum $\mathcal{S}(\mathcal{N})$ for a Schiff-like dipole moment has a more complicated nonlinear structure.

The correction terms from $\mathcal{S}(\mathcal{N})$, which involves the averages on RPA vacuum state are also determined using some considerations about the electron density. This approximation consists in using the generalized definition of the root mean square from nuclear physics, for the calculus of the averages for the radius powers on the RPA vacuum states. Such a model involves only one parameter, related to the thickness of the diffusion region. Due to the nuclear origin of this approach, the diffusion parameter a, to our knowledge, doesn't have an atomic equivalent, so that it could be considered as a free parameter that might be appropriately chosen. The thickness of the diffusion region is varying from one cluster to another. This statement is supported by the excellent results for static electric polarizabilities based on the calculations of the number of spilled out electrons from Ref. [10], which are situated exactly in the diffusion region discussed above. In order to identify the dependence of the diffusion parameter a on the number of atoms from the cluster, we determine for each cluster the value of a which corresponds to best agreement of the numerical values for the quantity $\mathcal{S}(\mathcal{N})$ with the direct calculated energy-weighted sum of the reduced transition probabilities. Further, the resulting values are interpolated with a parabola in the variable $\mathcal{N}^{1/3}$ (see Fig. 1). The parabola obtained in this way determines the diffusion

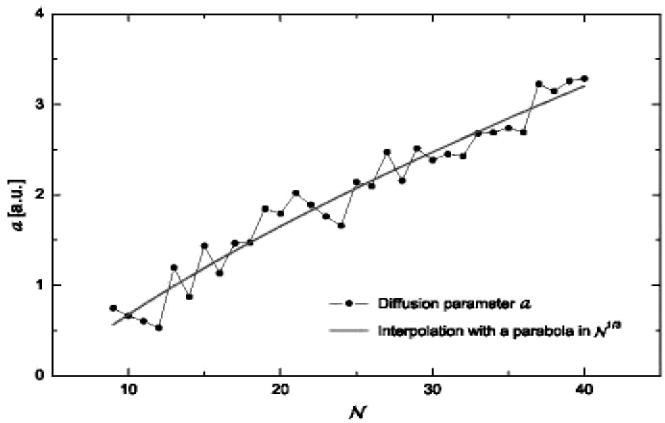

Fig. 1 – The diffusion parameter a (black circles), which reproduce numerical values of the left hand side of the equation (2.12), are interpolated with a parabola in variable $\mathcal{N}^{1/3}$: $a(\mathcal{N}) = -0.975157 - 0.0112138\mathcal{N}^{1/3} + 0.360518\mathcal{N}^{2/3}$.

Table I

The energy-weighted sum of the reduced dipole transition probabilities for all considered clusters are compared with the corresponding values of the quantity $\mathcal{S}(\mathcal{N})$ calculated by means of a RPA based approach and, alternatively, by using series expansion for the electron density. For the last one is also showed the diffusion parameter determined through interpolation for each number of atoms in cluster. Note that all three values for sum have a general increasing character with the number of atoms from cluster

Number of atoms $\mathcal{N}$	Diffusion parameter a [a.u.]	$S(\mathcal{N})$ [eV·Å$^2 \cdot e^2$] calculated with Eq. (4.5)	Left hand side of Eq. (2.12) [eV·Å$^2 \cdot e^2$]	$S(\mathcal{N})$ [eV·Å$^2 \cdot e^2$] calculated within RPA formalism
8	0.44449	466.6263	302.0624	910.0575
9	0.56139	575.6460	639.0365	1369.3987
10	0.67406	698.6136	693.5628	1518.2863
11	0.78306	835.9390	758.7141	1654.0512
12	0.88882	987.9623	820.5208	1777.3326
13	0.99170	1154.9717	1312.1053	2970.2716
14	1.09199	1337.2144	1178.2702	2387.2776
15	1.18993	1534.9054	1786.9321	3014.3080
16	1.28573	1748.2336	1597.1235	3390.2880
17	1.37957	1977.3664	2082.4288	3231.5732
18	1.47159	2222.4535	2223.7094	3328.1524
19	1.56194	2483.6294	2933.1139	3195.8121
20	1.65072	2761.0161	2994.3472	3275.4390
21	1.73805	3054.7245	3585.9781	3587.0177
22	1.82400	3364.8561	3491.4297	3665.1528
23	1.90867	3691.5043	3399.4747	3741.5237
24	1.99213	4034.7551	3356.1058	3816.6408
25	2.07444	4394.6881	4554.6071	4694.7566
26	2.15567	4771.3774	4617.6377	4580.9947
27	2.23586	5164.8920	5840.3050	5490.5231
28	2.31508	5575.2964	5129.7265	4333.7850
29	2.39337	6002.6501	6381.0278	5264.2589
30	2.47076	6447.0122	6170.2477	5783.8671
31	2.54731	6908.4339	6584.3887	5453.5807
32	2.62303	7386.9662	6698.8377	5553.0120
33	2.69798	7882.6568	7809.2993	5936.5530
34	2.77218	8395.5507	8073.8570	6500.3696
35	2.84566	8925.6908	8483.1580	6155.7468
36	2.91844	9473.1177	8524.2718	6280.1866
37	2.99056	10037.8699	11162.4451	8094.2567
38	3.06203	10619.9844	11028.4490	8767.5443
39	3.13288	11219.4963	11851.6975	8438.3580
40	3.20313	11836.4391	12280.0742	8625.7552

parameter a in the range of 0.4–3.2 a.u. It is interesting that the dominant part of the interpolating parabola is represented by the square term, which reflects some surface features, judging from the $\mathcal{N}$ dependence of the cluster radius, $R = r_s\mathcal{N}^{1/3}$. The calculation of the quantity $\mathcal{S}(\mathcal{N})$ makes use of the values of a lying on the interpolating curve. In this way the sum $\mathcal{S}(\mathcal{N})$ will depend only on the number of atoms by means of a sixth order polynomial in $\mathcal{N}^{1/3}$.

In Table I, we presented the values of the energy-weighted sum of the reduced dipole transition probabilities for all clusters considered in this work. These results are compared with those calculated with analytical expressions of the quantity $\mathcal{S}(\mathcal{N})$ obtained with two approaches: based on the RPA results and from electron density considerations. Concerning the calculations based on the electron density, the diffusion parameter $a(\mathcal{N})$ determined from the interpolation is also listed for each cluster.

In Fig. 2 and 3 we show the sum $\mathcal{S}(\mathcal{N})$ calculated by the RPA approach and density expansion method respectively, as function of the number of atoms. These are compared with the energy weighted sum calculated by RPA formalism using a projected spherical single particle basis. An excellent agreement is obtained between the energy-weighted sum of the reduced dipole transition probabilities with the numerical value of the quantity $\mathcal{S}(\mathcal{N})$ calculated on the electron density considerations (see Fig. 2). This is due to the presence of a free parameter in the analytical expression

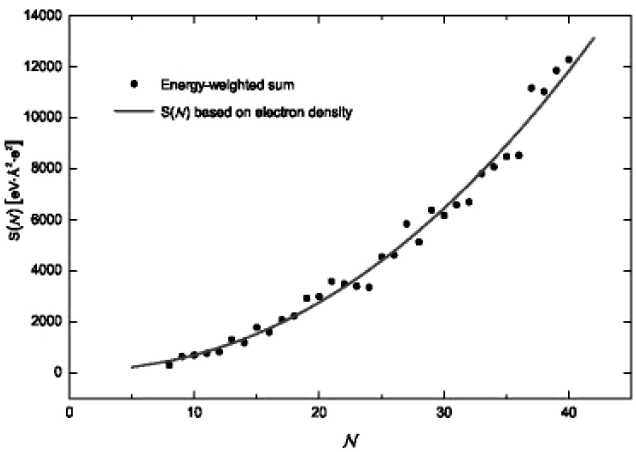

Fig. 2 – The calculated energy-weighted sums of the reduced dipole transition probabilities (black circles) for *Na* clusters with 8–40 atoms are compared with the numerical results of $\mathcal{S}(\mathcal{N})$ given by Eq. (4.5) and represented by a solid line.

of $\mathcal{S}(\mathcal{N})$ in this model, namely, the diffusion parameter a, fact which allowed us to improve the results corresponding to the situation without the correction term depending on the diffusion parameter in the Eq. (4.1). Note that the results of the same model but without the consideration of corrections related to the diffusion character of the electronic density are still in good agreement with direct calculated energy-weighted sum of reduced dipole transition probabilities.

It is interesting to mention that also the RPA based calculations of the $\mathcal{S}(\mathcal{N})$ are very close to the direct calculated sum for a large range of the clusters. From Fig. 3, one can be seen that the largest discrepancies are met for the light clusters and smaller for clusters with $\mathcal{N} \geq 28$. The intermediate region of clusters is characterized by a good agreement between the compared quantities.

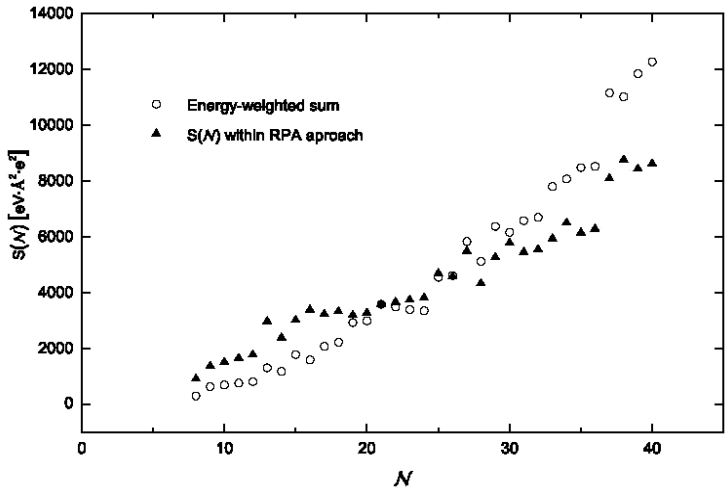

Fig. 3 – The calculated energy-weighted sums of the reduced dipole transition probabilities (open circles) for *Na* clusters with 8–40 atoms are compared with the numerical results of $\mathcal{S}(\mathcal{N})$ given by the RPA approach (black triangles).

Analyzing the numerical results obtained for both approaches, one may assert that the dipole moment of the Schiff form satisfies a modified TRK sum rule. Actually this confirms the consistency of the many body approach used in Ref. [10] for describing the dipole collective excitations in the *Na* clusters.

VI. SUMMARY

In the previous sections was showed that the Schiff-like dipole moment used in the calculation of the photoabsorbtion cross section spectra of the *Na* clusters, presented in a previous paper [10], satisfies an extended TRK sum rule. The main

features which led us to this statement can be summarized as follows. First of all, the RPA energy-weighted sum of the reduced dipole transition probabilities, with a Schiff-like dipole moment, was calculated. For the reduced probabilities analytical expressions depending on the RPA forward-going and backward-going amplitudes have been used. Numerical values of this energy-weighted sum are therefore compared with results provided by the right hand side of the sum rule equation (2.12), which is represented by a double commutator of the modified dipole moment operator and the system Hamiltonian. The double commutator is analytically calculated. Thus, the final result for the right hand side of our dipole sum rule consists of three terms, one corresponding to the simple dipole TRK sum rule and another two correction terms which imply averages of the radius powers with the RPA vacuum state.

Hence, the main effort in evaluating the right hand side of the sum rule, denoted by $\mathcal{S}(\mathcal{N})$, is to compute the radius power averages with the RPA vacuum state. This is achieved by using two different approaches: one is based on the RPA results and another one is using an electron density expansion around the jellium sphere radius.

The r^2 and r^4 averages corresponding to the RPA vacuum, are expressed in terms of the RPA phonon amplitudes and the *pp* and *hh* single particle matrix elements of the mentioned operators.

The successful description of the static electric polarizabilities with the help of the number of spilled out electrons [10], inspired us to use a phenomenological expression for the electron density, to calculate the average values of r^2 and r^4, respectively. In this model, the electron density is supposed not going sharply to zero at the cluster surface, but decreasing gradually and thus defining a diffusion region were the spilled out electrons are localized. In this way the average of the radius powers can be approximated by a series expansion in terms of $\frac{a}{R}$ where a defines the thickness of the diffusion region and R is the cluster radius. Such an approximation suggests that the quantity $\mathcal{S}(\mathcal{N})$ depends only on $\mathcal{N}$ and one free parameter, which is the diffusion parameter. The freedom of this parameter is coming from the fact that the thickness of diffusion region is not constant for all clusters, contrary to the nuclear case from where the model originated. Interpolating the values of the diffusion parameter which provide the best agreement with the numerical results for the energy-weighted sum of the reduced dipole transition probabilities, an explicit dependency of the quantity $\mathcal{S}(\mathcal{N})$ on the number of atoms in cluster is obtained. The numerical results, within this model, are in excellent agreement with the energy-weighted sum of reduced probabilities. It is worth noting, that this approach provides an analytical expression of the quantity $\mathcal{S}(\mathcal{N})$ depending on universal and structure constants which, as a matter of fact, is indeed consistent with the definition of the sum rule.

It is noteworthy to mention that the RPA based calculations of the quantity $\mathcal{S}(\mathcal{N})$ are also consistent with those from energy-weighted summation of the transition probabilities. This fact supports our option for using the RPA formalism for description of the many body properties of the atomic clusters.

The final conclusion is that the numerical results for both approaches presented here confirm the fact that the Schiff-like dipole moment used for the RPA description of the photoabsorbtion cross section spectrum, satisfies an extended TRK dipole sum rule. The saturation of the extended sum rule is a positive test for the single particle basis as well as for the dimension of the dipole *ph* space involved in the RPA description.

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VII. APPENDIX A

Here we present the explicit derivation of the right hand side of the Eq. (2.12), which defines the sum rule for the adopted modified dipole moment

$$\sum_n (E_n - E_0)\left|\langle 0\|\mathcal{M}(E1)\|1_n\rangle\right|^2 = \frac{3}{2}\langle 0|\left\|\left[\left[\mathcal{M}(E1), H\right], \mathcal{M}(E1)\right]\right||0\rangle. \tag{A.1}$$

The Hamiltonian of a many body system have the general form

$$\hat{H} = \sum_{\alpha=1}^{\mathcal{N}} \frac{p_\alpha^2}{2m_e} + \sum_{\alpha\neq\beta}^{\mathcal{N}} V_{\alpha\beta}(\vec{r}), \tag{A.2}$$

where $\mathcal{N}$ is the number of components from the system. V is the two body potential associated to the mutual interaction between components of the system, and it commutes with the dipole moment (2.8), such that the sum rule (A.1) becomes

$$\sum_n (E_n - E_0)\left|\langle 0\|\mathcal{M}(E1)\|1_n\rangle\right|^2 = \frac{1}{2}\sum_{\alpha=1}^{\mathcal{N}}\langle 0|\left\|\left[\left[\mathcal{M}(E1), \frac{p_\alpha^2}{2m_e}\right], \mathcal{M}(E1)\right]\right||0\rangle. \tag{A.3}$$

In order to calculate the double commutator from the right hand side of the above equation, the Cartesian representation of the space and momentum operator components is adopted. The modified dipole moment operator of the Schiff form, written in this way is

$$\mathcal{M}(E1) = e\sum_i \left(x_i - \frac{3}{5r_s^2}\sum_j x_j^2 x_i\right)\vec{n}_i, \tag{A.4}$$

where $\vec{n}_i$ are the unit vectors of the principal axes of the coordinate system. The first commutator of the modified dipole moment with the kinetic energy is as follows

$$\left[\mathcal{M}(E1),\frac{p^2}{2m_e}\right]=\left[e\sum_i\left(x_i-\frac{3}{5r_s^2}\sum_j x_j^2x_i\right),\sum_k\frac{p_k^2}{2m_e}\right]\cdot\vec{n}_i$$
$$=\frac{e}{2m_e}\sum_{ik}\left\{\left[x_i,p_k^2\right]-\frac{3}{5r_s^2}\sum_j\left[x_j^2x_i,p_k^2\right]\right\}\vec{n}_i. \tag{A.5}$$

Using the basic commutation relation of the space and momentum components $[p_i, x_i]=-i\hbar\delta_{ij}$, the above commutator becomes

$$\left[\mathcal{M}(E1),\frac{p^2}{2m_e}\right]=\frac{e}{2m_e}\sum_{ik}\left\{-2i\hbar\delta_{ik}p_k-\frac{3}{5r_s^2}\sum_j(-2i\hbar)\left[x_j^2p_k\delta_{ik}+\delta_{jk}\left(x_jp_k+p_kx_j\right)x_i\right]\right\}\vec{n}_i$$
$$=\frac{i\hbar e}{m_e}\sum_i\left\{p_i-\frac{3}{5r_s^2}\sum_j\left[x_j^2p_i+\left(x_jp_j+p_jx_j\right)x_i\right]\right\}\cdot\vec{n}_i. \tag{A.6}$$

Thus, on the base of last result, the double commutator can be computed following the procedure:

$$\left[\left[\mathcal{M}(E1),\frac{p^2}{2m_e}\right],\mathcal{M}(E1)\right]=$$
$$=-\frac{i\hbar e^2}{m_e}\sum_{il}\left[\left\{p_i-\frac{3}{5r_s^2}\sum_j\left[x_j^2p_i+\left(x_jp_j+p_jx_j\right)x_i\right]\right\},\left(x_l-\frac{3}{5r_s^2}\sum_j x_m^2x_l\right)\right]\underbrace{\left(\vec{n}_i\cdot\vec{n}_l\right)}_{\delta_{il}}$$
$$=-\frac{i\hbar e^2}{m_e}\sum_i\left[\left\{p_i-\frac{3}{5r_s^2}\sum_j\left[x_j^2p_i+\left(x_jp_j+p_jx_j\right)x_i\right]\right\},\left(x_i-\frac{3}{5r_s^2}\sum_m x_m^2x_i\right)\right]$$
$$=-\frac{i\hbar e^2}{m}\sum_i\left[T_i^1+T_i^2+T_i^3+T_i^4\right]$$

where the terms T_i^1, T_i^2, T_i^3, T_i^4 have the expressions:

$$T_i^1=\left[p_i,x_i\right]=i\hbar, \tag{A.7}$$

$$T_i^2=-\frac{3}{5r_s^2}\sum_m\left[p_i,x_m^2x_i\right]=-\frac{3i\hbar}{5r_s^2}\sum_m\left(x_m^2+2x_mx_i\delta_{im}\right)=-\frac{3i\hbar}{5r_s^2}\left(r^2+2x_i^2\right), \tag{A.8}$$

$$T_i^3=-\frac{3}{5r_s^2}\sum_j\left[\left[x_j^2p_i+\left(x_jp_j+p_jx_j\right)x_i\right],x_i\right]$$
$$=-\frac{3i\hbar}{5r_s^2}\sum_j\left(x_j^2+2x_jx_i\delta_{ij}\right)=-\frac{3i\hbar}{5r_s^2}\left(r^2+2x_i^2\right), \tag{A.9}$$

$$
\begin{aligned}
T_i^4 &= \frac{9}{25r_s^4}\sum_{jm}\left[\left[x_j^2 p_i + \left(x_j p_j + p_j x_j\right)x_i\right], x_m^2 x_i\right] \\
&= \frac{9i\hbar}{25r_s^4}\sum_{jm}\left(x_j^2 x_m^2 + 2x_j^2 x_i x_m \delta_{im} + 2x_m^2 x_j x_i \delta_{ij} + 4x_i^2 x_j x_m \delta_{jm}\right) \\
&= \frac{9i\hbar}{25r_s^4}\left(r^4 + 8r^2 x_i^2\right).
\end{aligned}
\tag{A.10}
$$

The final result for the double commutator from Eq. (A.3) is

$$
\begin{aligned}
\left[\left[\mathcal{M}(E1), \frac{p^2}{2m_e}\right], \mathcal{M}(E1)\right] &= -\frac{i\hbar e^2}{m_e}\sum_k\left[i\hbar - \frac{6i\hbar}{5r_s^2}\left(r^2 + 2x_k^2\right) + \frac{9i\hbar}{25r_s^4}\left(r^4 + 8r^2 x_k^2\right)\right] \\
&= \frac{3\hbar^2 e^2}{m_e}\left[1 - 2\frac{r^2}{r_s^2} + \frac{33}{25}\frac{r^4}{r_s^4}\right].
\end{aligned}
\tag{A.11}
$$

Using this expression for the double commutator of the Hamiltonian of the system with the Schiff-like dipole moment operator and particularizing it to the case of valence electrons from the cluster, the RPA sum rule for this dipole operator will have the form

$$
\sum_n \left(E_n - E_0\right)\left|\langle 0 \| M(\vec{r}) \| 1_n \rangle\right|^2 = \frac{9\hbar^2 e^2}{2m_e}\sum_{\alpha=1}^{\mathcal{N}}\left[1 - \frac{2}{r_s^2}\langle 0 \| r_\alpha^2 \| 0 \rangle + \frac{33}{25r_s^4}\langle 0 \| r_\alpha^4 \| 0 \rangle\right], \tag{A.12}
$$

which is just the Eq. (2.12).

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