Random-phase approximation in a local representation

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The random-phase approximation (RPA) in Q-P representation is introduced. It is shown that the RPA equations can be regained from varying the ratio of energy-weighted moments $m_3(Q)/m_1(Q)$ with respect to the particle-hole operator Q. In particular, a restricted set of *local* operators $Q(\mathbf{r})$ is discussed, leading to a hydrodynamic approximation to the RPA. The practical solution of the collective eigenvalue problem for a given multipolarity proceeds via a power expansion of $Q(\mathbf{r})$ and the solution of a secular equation for coupled modes. As an application of our method, we discuss collective dipole vibrations (plasmons) in small spherical metal clusters.

I. INTRODUCTION

The random-phase approximation (RPA) has been, since long ago,[1] the most widely used method for a microscopic treatment of small-amplitude excitations in all sorts of many-body systems. There are many different ways to derive the RPA: diagrammatic techniques, time-dependent Hartree-Fock, and Green's-function methods, etc. The reader may refer to almost any standard textbook in many-body quantum mechanics for one or various representations of the RPA and its application. The RPA has helped very much in understanding microscopically the occurrence of collective modes in many-body systems, such as the plasmons in the electron gas or the phonons in liquid ^{3}He and in nuclei. Just recently, there has been a growing interest in a new area of research where collective modes appear in a finite fermion system: electronic excitations in small metallic clusters.[2−4] Collective modes, on the other hand, often have a very simple structure that allows one to compute them in simpler approximations to the full RPA, such as, e.g., the sum-rule[5] and the hydrodynamical (or "fluid dynamical") approaches.[6,7]

It is the aim of this paper to show how approximations to the RPA can be constructed systematically by variation in restricted spaces of excitation operators. To that end, we introduce a representation of the RPA in terms of coordinatelike operators Q and momentumlike operators P that is more adapted for intuitive guesses of collective approximations. Since it is usually easier to make good guesses for the Q operators, we derive a variational principle for mere Q variation. We then discuss in particular a "local RPA" where the coordinatelike operators Q are restricted to being local one-body operators. This leads to a differential equation for collective flow quite similar to the hydrodynamical equations. As a more practicable alternative, we introduce a momentum expansion of the local collective Q operator. The technique is exemplified for the case of collective dipole excitations (plasmons) of the electrons in small metallic clusters.

The paper is outlined as follows. In Sec. II we briefly review the RPA in terms of the equations-of-motion technique which is most appropriate for our purposes of variation in restricted spaces of excitation operators. In Sec. III we derive the variational principle for Q variation and introduce the local RPA. In Sec. IV we present the model and calculations for plasmons in metallic clusters.

II. SHORT REVIEW OF RPA ALGEBRA

A. The equations-of-motion technique

Out of the many possible derivations of the RPA, we use here the equations-of-motion technique which formulates the many-body dynamics in terms of an algebra of excitation operators.[8] Let a many-particle system be given in a state $|\Psi\rangle$, usually the ground state. The excitations about the state $|\Psi\rangle$ are to be described by a chosen set of elementary operators

$$\{ A_\alpha^\dagger, \alpha = 1, \ldots, M \} \ . \tag{1}$$

The operator which creates an excited state $|\Psi_n\rangle = C_n^\dagger |\Psi\rangle$ is superposed from these elementary operators

$$C_n^\dagger = c_n^\alpha A_\alpha^\dagger \ , \tag{2}$$

where we use Einstein's sum convention that any pair of upper and lower indices is to be summed over. The superposition coefficients c_n^α are determined such that the operator equation $[H, C_n^\dagger] = \hbar\omega_n C_n^\dagger$ is fulfilled "on the average," i.e.,

$$\langle \Psi | [\delta C, [H, C_n^\dagger]] | \Psi \rangle = \hbar\omega_n \langle \Psi | [\delta C, C_n^\dagger] | \Psi \rangle \ , \tag{3}$$

where the δC runs over all operators of the algebra

$$\delta C \in \{ A_\alpha, \alpha = 1, \ldots, M \} \ . \tag{4}$$

There are as many equations as there are coefficients and this usually suffices to determine uniquely the c_n^α. There may be exceptions for spurious modes, but these can easi-

ly be pinned down in most cases.

Note that the equation of motion (3) can be derived from the Ritz variational principle of minimal (or stationary) energy

$$\hbar\omega_n = \langle \Psi|[C_n,[H,C_n^\dagger]]|\Psi\rangle \tag{5}$$

under the constraint of proper orthonormalization

$$\langle \Psi|[C_m,C_n^\dagger]|\Psi\rangle = \delta_{nm}, \quad \langle \Psi|[C_m,C_n]|\Psi\rangle = 0 . \tag{6}$$

Using the orthonormalization (6) and the fact that the δC may run equally well over all C_m, one can rewrite Eq. (3) in the form

$$\langle \Psi|[C_m,[H,C_n^\dagger]]|\Psi\rangle = \delta_{nm}\hbar\omega_m , \tag{7}$$

which means that the $C_n^\dagger$ diagonalize H in the algebra (1).

All expressions above are already written in terms of commutators and double commutators. This implies that the ground state $|\Psi\rangle$ is a vacuum for the $C_n^\dagger$ excitations, i.e.,

$$C_n|\Psi\rangle = 0 \tag{8}$$

for all n. Thus excitations and the structure of the ground state are related to each other. Possible consequences are exemplified for the RPA in Sec. II B. The energy in the form (5) casts all dynamical information onto the evaluation of the double commutator with H. This is most appropriate for an algebraic approach, because it brings the emerging dynamical equations for $C_n^\dagger$ into the typical quantum-mechanical form of commutator equations for the operators. As a further bonus, the double commutators make the remaining expectation value much less sensitive to the structure of $|\Psi\rangle$, allowing for drastic approximation in that place.

B. RPA in equations-of-motion formulation

The RPA is easily derived within the framework of the equations-of-motion technique by selecting as a basis the algebra of one-particle–one-hole (1p-1h) operators:

$$A_\alpha^\dagger \equiv A_{ph}^\dagger \in \{a_p^\dagger a_h, a_h^\dagger a_p\} , \tag{9}$$

where p represents particle states and h represents hole states. The label α accounts for two indices p and h, the $a^\dagger$ are fermion creation operators, and the a are fermion annihilation operators. The expansion coefficients for particle-hole states and those for hole-particle states are often distinguished. A standard form for the excitation operator is then

$$C_n^\dagger = \sum_{p,h} (x_n^{ph} a_p^\dagger a_h - y_n^{ph} a_h^\dagger a_p) , \tag{10}$$

and the RPA equations become coupled equations for the coefficients x and y which are easily derived from the variational equation (3) whereby δC runs over all elementary excitations (9), namely, $a_p^\dagger a_h$ and $a_h^\dagger a_p$.

Note that the hole-particle operator $a_h a_p$ is inactive if it acts on a Hartree-Fock state, because there is no particle state to annihilate. But we have seen already above that $|\Psi\rangle$ is, in principle, a correlated ground state defined

as the vacuum of excitations, see Eq. (8). With the choice of the algebra (9) we obtain thus the RPA-correlated ground state. It can be built with $2p$-$2h$ and higher correlations on top of the basic Hartree-Fock state Φ_0, i.e.,

$$|\Psi\rangle = \left[1 + \sum_{p,p',h,h'} \gamma^{pp'hh'} a_p^\dagger a_{p'}^\dagger a_h a_{h'} \cdots \right]|\Phi_0\rangle . \tag{11}$$

The expansion coefficients γ can be computed from the RPA coefficients x_n^{ph} and y_n^{ph}. (For details and for an extensive discussion of possible pitfalls, see Ref. 9.)

One usually assumes that the correlations are small, i.e., $|\gamma| \ll 1$. The double commutators in the RPA equations of motion, e.g., Eq. (3), are particularly insensitive to the correlations. In fact, they are of order γ^2. Thus one neglects the correlations in evaluating the expectation values of double commutators, e.g., for the energy

$$\hbar\omega_n = \langle \Psi|[C_n,[H,C_n^\dagger]]|\Psi\rangle \simeq \langle \Phi_0|[C_n,[H,C_n^\dagger]]|\Phi_0\rangle . \tag{12}$$

This is called the *quasiboson* approximation.[8] We will employ it throughout in the following considerations.

It is obvious that ph operators play a central role in RPA. Not all the operators are immediately pure ph operators, and one needs to pick the ph part of it. This may be done by

$$\mathcal{O}_{ph} = \sum_{p,h} (a_p^\dagger a_h \langle \Phi_0|[a_h^\dagger a_p, \mathcal{O}]|\Phi_0\rangle$$
$$-a_h^\dagger a_p \langle \Phi_0|[a_p^\dagger a_h, \mathcal{O}]|\Phi\rangle) , \tag{13}$$

or by using the recoupled basis

$$\mathcal{O}_{ph} = \sum_n (C_n^\dagger \langle \Psi|[C_n, \mathcal{O}]|\Psi\rangle - C_n \langle \Psi|[C_n^\dagger, \mathcal{O}]|\Psi\rangle) \tag{14}$$

for any operator $\mathcal{O}$. In practical evaluations, one often has simpler accesses to the ph part; the above expressions are most useful for formal purposes. For example, one can rewrite the RPA equation (7) as an operator equation projected into ph space:

$$[H,C_n^\dagger]_{ph} = \hbar\omega C_n^\dagger . \tag{15}$$

C. RPA moments and sum rules

Excitation spectra of many-body systems are often analyzed[5] in terms of the moments $m_k(Q)$ of the strength function $S_Q(E)$ for a given external excitation operator Q:

$$m_k(Q) = \int_0^\infty E^k S_Q(E)dE = \sum_{n(\neq 0)} (\hbar\omega_n)^k |\langle \Psi_n|Q|\Psi\rangle|^2 . \tag{16}$$

The moment m_{-1}, for example, is half the static polarizability [see Eq. (23) below], and the moment m_1 describes the energy-weighted sum rule which plays a key role in photoabsorption cross sections.

The odd moments (with $k > 0$) can be expressed by multiple commutators of Q with H, and their expectation values in the RPA state $|\Psi\rangle$ are rather insensitive to

ground-state correlations, which allows us to evaluate them in the quasiboson approximation. In particular, the so-called *equivalence theorems*

$$m_1^{\text{RPA}}(Q) = \sum_{n(\neq 0)} (\hbar\omega_n) |\langle \Psi_n | Q | \Psi \rangle|^2$$

$$= \tfrac{1}{2} \langle \Phi_0 | [Q, [H, Q]] | \Phi_0 \rangle , \qquad (17)$$

$$m_3^{\text{RPA}}(Q) = \sum_{n(\neq 0)} (\hbar\omega_n)^3 |\langle \Psi_n | Q | \Psi \rangle|^2$$

$$= \tfrac{1}{2} \langle \Phi_0 | [[H, Q], [H, [Q, H]]] | \Phi_0 \rangle \qquad (18)$$

were shown by Thouless[10] to hold *exactly* if the interaction in H is density independent. For interactions which depend on the density, they hold[5] within the quasiboson approximation, i.e., neglecting terms of second order in the amplitude γ of the ground-state correlations [see Eq. (11)]:

$$m_1^{\text{RPA}}(Q) = \tfrac{1}{2} \langle \Psi | [Q, [H, Q]] | \Psi \rangle$$

$$= \tfrac{1}{2} \langle \Phi_0 | [Q, [H, Q]] | \Phi_0 \rangle + O(\gamma^2) , \qquad (19)$$

and analogously for $m_3^{\text{RPA}}(Q)$.

In our development further below, we will encounter multiple commutators of the form appearing in Eqs. (17) and (18), but containing a pair of different operators Q_α, Q_β. They can be derived from the moments $m_k(Q_\alpha, Q_\beta)$ of a mixed strength function by

$$m_k(Q_\alpha, Q_\beta) = \sum_{n(\neq 0)} (\hbar\omega_n)^k \langle \Psi | Q_\alpha^\dagger | \Psi_n \rangle \langle \Psi_n | Q_\beta | \Psi \rangle .$$

$$(20)$$

Indeed, it has been shown[5] that the above equivalence theorems [(17) and (18)] can be generalized, within the quasiboson approximation, to the corresponding expressions including the mixed moments:

$$m_1^{\text{RPA}}(Q_\alpha, Q_\beta) = \tfrac{1}{2} \langle \Phi_0 | [Q_\alpha, [H, Q_\beta]] | \Phi_0 \rangle , \qquad (21)$$

$$m_3^{\text{RPA}}(Q_\alpha, Q_\beta) = \tfrac{1}{2} \langle \Phi_0 | [[H, Q_\alpha], [H, [Q_\beta, H]]] | \Phi_0 \rangle .$$

$$(22)$$

The inverse energy-weighted RPA sum $m_{-1}(Q)$ is related[11] to the static polarizability $\alpha(Q)$ and given by

$$m_{-1}^{\text{RPA}}(Q) = \tfrac{1}{2} \alpha(Q)$$

$$= \frac{1}{2} \frac{d}{d\lambda} \langle \lambda | Q | \lambda \rangle \bigg|_{\lambda=0} = \frac{1}{2} \frac{d^2}{d\lambda^2} \langle \lambda | H \lambda \rangle \bigg|_{\lambda=0} ,$$

$$(23)$$

where $|\lambda\rangle$ is the solution of the *static constrained* Hartree-Fock variational calculation

$$\delta \langle \lambda | H - \lambda Q | \lambda \rangle = 0 . \qquad (24)$$

Note that no analogous equivalence theorems exist for the moments m_k with *even* k because these are very sensitive to ground-state correlations. The *odd* moments m_k—we shall henceforth omit the superscript "RPA"—therefore play a key role in the so-called *sum-rule approach* to the RPA. There one guesses some collective excitation operator Q and evaluates average spectral properties from the associated moments $m_{-1}, m_1,$ and m_3. To this purpose, it is useful to define the following energies:

$$E_k(Q) = [m_k(Q) / m_{k-2}(Q)]^{1/2} . \qquad (25)$$

It can be shown[5] that for the centroid (i.e., mean energy) $\bar{E}$ and the variance σ of the strength distribution $S_Q(E)$, defined by

$$\bar{E} = m_1/m_0, \quad \sigma^2 = m_2/m_0 - (m_1/m_0)^2 , \qquad (26)$$

the following inequalities hold:

$$E_1 \leq \bar{E} \leq E_3, \quad \sigma \leq \tfrac{1}{2}(E_3^2 - E_1^2)^{1/2} . \qquad (27)$$

This allows us to estimate the mean energy and width of a RPA spectrum in terms of the simple ground-state expectation values in Eqs. (17) and (18), instead of their much more elaborate calculation in terms of the exact and even RPA moments.

The operator Q is usually chosen to be local: $Q = Q(\mathbf{r})$; in most cases simply as the multipole operator $Q \sim r^L Y_{LM}(\theta, \phi)$ for $L \geq 1$, or as $Q \sim r^2$ (for $L = 0$). The above sum-rule estimates give a rather simple and reliable picture of the collective excitations of a many-body system, e.g., the giant resonances in nuclei,[12] if most of the collective strength is concentrated in a more or less narrow energy region. Nevertheless, it is possible to improve on the description by not just guessing one operator Q, but by coupling several different operators (see, e.g., Refs. 13 and 14). To this end, it is advantageous to rewrite the RPA equations in terms of Hermitian and conjugate operators Q and P; this will be done in the next subsection.

For local operators $Q(\mathbf{r})$, the RPA moments m_1 and m_3 have a simple physical interpretation in terms of the so-called *scaling* concept: the scaling deformation operator $e^{-\beta[H,Q]}$ generates a collective path with deformation label β. The moment m_3 can then be related to a stiffness parameter (spring constant) $\mathcal{H}$ and the moment m_1 to an inertial parameter $\mathcal{B}$ for a deformation dynamics in terms of β. $\mathcal{B}$ is, in fact, the hydrodynamical collective mass corresponding to a displacement field $\mathbf{u} \sim \nabla Q$. The energy E_3 discussed above is in that notion nothing else than a harmonic oscillator energy

$$E_3 = (m_3/m_1)^{1/2} = \hbar\omega_{\text{scal}} = \sqrt{\mathcal{H}/\mathcal{B}} . \qquad (28)$$

(See Appendix A for the details of this scaling concept.)

D. RPA in Q, P description

The sum-rule approach puts emphasis on an operator Q which is a local and Hermitian operator, i.e., $Q = Q(\mathbf{r})$. More generally, Q is considered to be a time-even and Hermitian operator; it serves, so to speak, as a generalized RPA coordinate and is to be complemented by its momentum conjugate P which is a time-odd Hermitian operator. One can easily formulate the RPA in terms of Q and P operators rather than $C_n^\dagger$ and C_n. This provides

a flexible starting point for extended sum-rule approaches and local approximations to the RPA. Good time parity for Q and P is guaranteed for ground states $|\Psi\rangle$ which themselves have good time parity and which, in particular, are time even. This will always be assumed in the following.

In order to rewrite the RPA in Q,P form, we recouple the usual quasiboson operators $C_\alpha^\dagger$ and C_α to

$$Q_n = \frac{1}{\sqrt{2}}(C_n^\dagger + C_n), \quad P_n = \frac{i}{\sqrt{2}}(C_n^\dagger - C_n), \tag{29}$$

where Q_n is a Hermitian and time-*even* $1p$-$1h$ operator and P_n is a Hermitian and time-*odd* $1p$-$1h$ operator. The index n labels the RPA spectrum. A microscopic expansion in terms of single-particle operators a_p and a_h is

$$Q_n = \sum_{p,h} q_n^{ph}(a_p^\dagger a_h + a_h^\dagger a_p),$$

$$P_n = \sum_{p,h} p_n^{ph} i(a_p^\dagger a_h - a_h^\dagger a_p), \tag{30}$$

where p is a particle state and h a hole state. The coefficients q_n^{ph} and p_n^{ph} are related to the RPA coefficients x_n^{ph} and y_n^{ph} from Eq. (10) by equations similar to (29). The transformation (29) is orthogonal in the sense that the orthonormalization (6) leads to the conjugation relation

$$\langle \Phi_0 | [Q_n, P_m] | \Phi_0 \rangle = i\delta_{nm}. \tag{31}$$

(Note that $\langle \Phi_0 | [Q_n, Q_m] | \Phi_0 \rangle$ and $\langle \Phi_0 | [P_n, P_m] | \Phi_0 \rangle$ vanish for time-parity reasons.)

The variation of Q_n spans the complete set of *time-even* $1p$-$1h$ operators

$$\delta Q \in \{(a_p^\dagger a_h + a_h^\dagger a_p) \text{ for all } p,h\}, \tag{32}$$

whereas variation of P spans the complete set of *time-odd* $1p$-$1h$ operators

$$\delta P \in \{i(a_p^\dagger a_h - a_h^\dagger a_p) \text{ for all } p,h\}. \tag{33}$$

The expansion (30) is complete in the sense that the Q_n and P_n also span a complete set of $1p$-$1h$ operators. Thus one may consider alternatively $\delta Q \in \{Q_n \forall n\}$ and $\delta P \in \{P_n \forall n\}$.

A possible form of the RPA equations in Q,P representation is obtained by transforming Eq. (7), using $\langle \Phi_0 | [C_m, [H, C_n]] | \Phi_0 \rangle = 0$. The result resembles very much an oscillator algebra

$$\langle \Phi_0 | [Q_m, [H, Q_n]] | \Phi_0 \rangle = \delta_{nm} \mathcal{B}_n,$$

$$\langle \Phi_0 | [P_m, [H, P_n]] | \Phi_0 \rangle = \delta_{nm} \mathcal{C}_n, \tag{34}$$

from which the diagonal quantities $\mathcal{B}_n, \mathcal{C}_n$ can be readily computed. In fact, this is an algebra "on the average," and the expectation values over $|\Psi\rangle$ have been replaced by expectation values over $|\Phi_0\rangle$, exploiting again the quasiboson approximation (12). The RPA excitation energy of the mode n is then

$$\hbar\omega_n = (\mathcal{C}_n \mathcal{B}_n)^{1/2}. \tag{35}$$

Equations (34) suggest the interpretation of $\mathcal{C}_n$ as a spring constant of the mode n and of $\mathcal{B}_n$, here, as the according *inverse* inertial parameter. Note that this assignment is different from the one given in the sum-rule approach at the end of Sec. II C; it corresponds to a q-deformation path that is generated by the operator e^{-iqP} with the deformation label q. The equivalence of both pictures is discussed in more detail in Appendix A.

The ph projection (14) can also be reformulated in terms of the Q and P operators

$$\mathcal{O}_{ph} = \sum_n (iQ_n\langle\Psi|[P_n,\mathcal{O}]|\Psi\rangle - iP_n\langle\Psi|[Q_n,\mathcal{O}]|\Psi\rangle). \tag{36}$$

Thus one can derive from Eqs. (34) an alternative form of the RPA equations:

$$[H,Q_n]_{ph} = -i\mathcal{B}_n P_n,$$

$$[H,P_n]_{ph} = i\mathcal{C}_n Q_n. \tag{37}$$

We finally rewrite these equations as one single equation of second order in H for Q_n alone:

$$[H,[H,Q_n]_{ph}]_{ph} = (\hbar\omega_n)^2 Q_n. \tag{38}$$

This form will play a key role in the following considerations of a restricted RPA with pure Q variation.

III. RPA IN RESTRICTED Q SPACES

A. Regaining RPA from variation of Q

It is our aim to derive approximations to the RPA by variation of Q in restricted spaces, in particular using local operators $Q = Q(\mathbf{r})$. As a first step, we are going to show in this subsection that a free variation of Q alone can regenerate the full RPA equations.

First, we have to compute the RPA energy for *given* Q. (We omit in the present section the index n of the RPA mode, wherever we believe this not to cause confusion.) This proceeds in the following way: (i) compute the average inverse mass $\mathcal{B} = \langle \Phi_0 | [Q,[H,Q]] | \Phi_0 \rangle$; (ii) construct the conjugate momentum operator $P = i[H,Q]_{ph}/\mathcal{B}$; (iii) compute the average spring constant $\mathcal{C} = \langle \Phi_0 | [P,[H,P]] | \Phi_0 \rangle$. Thus the RPA energy, according to Eq. (35), becomes

$$\hbar\omega(Q) = \sqrt{\mathcal{C}\mathcal{B}}$$

$$= (\langle \Phi_0 | [P,[H,P]] | \Phi_0 \rangle \langle \Phi_0 | [Q,[H,Q]] | \Phi_0 \rangle)^{1/2}$$

$$= \left[\frac{\langle \Phi_0 | [[Q,H]_{ph},[H,[H,Q]_{ph}]] | \Phi_0 \rangle}{\langle \Phi_0 | [Q,[H,Q]] | \Phi_0 \rangle} \right]^{1/2} \tag{39}$$

$$= [m_3(Q)/m_1(Q)]^{1/2} = E_3(Q). \tag{40}$$

Now in a second step, we optimize the "prejudice" Q by making $E_3(Q)$ stationary, i.e., setting its first-order variation equal to zero:

$$\delta E_3(Q) = \delta\hbar\omega(Q) = \hbar\omega(Q + \delta Q) - \hbar\omega(Q) = 0. \tag{41}$$

From this condition and the expression (39) for the ener-

gy follows

$$\langle \Phi_0 | [[\delta Q, H]_{ph}, [H, [H, Q]_{ph}]] | \Phi_0 \rangle \mathcal{B}^{-1}$$
$$- \langle \Phi_0 | [\delta Q, [H, Q]] | \Phi_0 \rangle \mathcal{C} = 0 . \quad (42)$$

We employ

$$\langle \Phi_0 | [\delta Q, [H, Q]_{ph}] | \Phi_0 \rangle = \langle \Phi_0 | [[\delta Q, H]_{ph}, Q] | \Phi_0 \rangle$$

and collect to

$$\langle \Phi_0 | [[\delta Q, H]_{ph}, \{[H, [H, Q]_{ph}]_{ph} \mathcal{B}^{-1} - Q \mathcal{C}\}] | \Phi_0 \rangle = 0 .$$

Now we use the fact that

$$\{[\delta Q, H]_{ph}\} \propto \delta P \in \{A_{ph}^{\dagger} - A_{ph}\} ,$$

i.e., δP is from a complete set of time-odd $1p$-$1h$ operators, and obtain

$$[H, [H, Q]_{ph}]_{ph} = (\mathcal{B}\mathcal{C})Q , \quad (43)$$

which is exactly the RPA equation in the form (38). Strictly speaking, the unrestricted variation of Q leads to the RPA state with the *lowest* excitation energy. Using an orthogonalization procedure, one can then successively obtain the full RPA spectrum of operators Q_n with energies $\hbar \omega_n$.

We conclude that the *full RPA equations* are regained by *free variation* (and orthogonalization) of the $1p$-$1h$ operator Q in the energy $E_3(Q) = [m_3(Q)/m_1(Q)]^{1/2}$. This, in turn, means that optimal approximations for *restricted* choices of Q are to be found by *restricted variation* of $E_3(Q)$. This is the variational principle which will be used in the following.

One may be surprised that the conjugate operator P has been completely eliminated in the above considerations. It is to be remarked that the variational principle (41) implies a particular model for P, namely, $P = i[H, Q]_{ph} / \mathcal{B}$. This, of course, is an obvious model and is well motivated within the RPA algebra.

B. Local RPA from $Q \equiv Q(\mathbf{r})$

We now derive the equation of motion for a *local RPA* where the operator Q is restricted to be a *local function* $Q \equiv Q(\mathbf{r})$. Variation of m_3/m_1 with respect to $Q(\mathbf{r})$ yields

$$\langle \Phi_0 | [[\delta Q, H], [H, [H, Q]]] | \Phi_0 \rangle$$
$$- (\hbar \omega)^2 \langle \Phi_0 | [\delta Q, [H, Q]] | \Phi_0 \rangle = 0 , \quad (44)$$

where δQ runs over all possible spatial variations of $Q(\mathbf{r})$. One may take, for example, $\delta Q = \delta^3(\mathbf{r} - \mathbf{r}_0)$, where $\mathbf{r}_0$ runs over all positions in coordinate space. The Hamiltonian

H is assumed to consist of kinetic energy and a density-dependent, direct two-body force such that the total energy functional becomes

$$\mathcal{E} = \int d^3 r \left[\frac{\hbar^2}{2m} \tau + \mathcal{U}(\rho) \right] , \quad (45)$$

where ρ is the local density and $\tau = \sum_h \nabla \varphi_h^{\dagger} \cdot \nabla \varphi_h$ is the kinetic energy density (expressed here explicitly in terms of the occupied single-particle states φ_h).

The local Q commutes with the potential and we can easily evaluate (see also Appendix A)

$$[H, Q]_{ph} = [T, Q] = S = -\frac{\hbar^2}{2m} \{\nabla Q, \cdot \nabla\} . \quad (46)$$

The ph projection is unproblematic here because the kinetic energy is a one-body operator and the commutator of two one-body operators is again a one-body operator. It would remain to separate the ph part of $[H, Q]$ from the pp and hh part. But the latter cancel anyway[15] in evaluating the expectation value of the double commutator $[S[H, S]]$ in the ground state $| \Phi_0 \rangle$. Therefore the above expression suffices, and we obtain

$$[\delta Q, H] = -\delta S = \frac{\hbar^2}{2m} \{\nabla \delta Q, \cdot \nabla\} . \quad (47)$$

Furthermore, we can rewrite the second term in Eq. (44) as

$$\langle [\delta Q, [H, Q]] \rangle = -\frac{\hbar^2}{2m} \langle [\delta Q, \{\nabla Q, \cdot \nabla\}] \rangle \quad (48)$$
$$= \frac{\hbar^2}{m} \langle \nabla \delta Q \cdot \nabla Q \rangle .$$

Thus the task of variation with respect to $Q(\mathbf{r})$ can be replaced completely by the task of varying the associated displacement field

$$\mathbf{u} = -\frac{\hbar^2}{m} \nabla Q , \quad (49)$$

according to the variational equation

$$\langle [\tfrac{1}{2}\{\delta \mathbf{u}, \cdot \nabla\}, [H, \tfrac{1}{2}\{\mathbf{u}, \cdot \nabla\}]] \rangle - \omega^2 \langle \delta \mathbf{u} \cdot \mathbf{u} \rangle = 0 , \quad (50)$$

where

$$\delta \mathbf{u} = -\frac{\hbar^2}{m} \nabla \delta Q . \quad (51)$$

We now give a short sketch of the structure of the differential equation for $\mathbf{u}(\mathbf{r})$ derived from Eq. (50). We consider an energy functional of the form (45). Evaluating the double commutator in Eq. (50), we obtain the variational equation in the form

$$\int d^3 r \, \delta \mathbf{u}_i \cdot \left[\frac{\hbar^2}{m} [(\nabla_i \nabla_j \mathbf{u}_k) \tilde{\tau}_{kj} + \nabla_k (\nabla_j \mathbf{u}_k) \tilde{\tau}_{ji} + \nabla_j (\nabla_j \mathbf{u}_k) \tilde{\tau}_{ki} + \nabla_k \nabla_j (\nabla_i \nabla_j \mathbf{u}_k) \rho] \right.$$

$$\left. - \left[\mathbf{u}_k (\nabla_i \nabla_k v) \rho + (\nabla_i \mathbf{u}_k)(\nabla_k v) \rho + (\nabla_i \rho) \frac{\partial^2 \mathcal{U}}{\partial \rho^2} \mathbf{u}_k (\nabla_k \rho) \right] \right] = (\hbar \omega)^2 \int d^3 r \, \rho \delta \mathbf{u}_i \cdot \mathbf{u}_i ,$$

where we have introduced the kinetic-energy density tensor $\tilde{\tau}_{ij}$ by

$$\bar{\mathcal{T}}_{ij} = 4 \sum_{\alpha} (\nabla_i \varphi_\alpha)^\dagger (\nabla_j \varphi_\alpha) - \nabla_i \nabla_j \rho \ ,$$

and the mean field v is given by

$$v = \frac{\partial \mathcal{U}}{\partial \rho} \ .$$

The most general variation of $\mathbf{u}$ is

$$\delta \mathbf{u} = \mathbf{e}_q \delta(\mathbf{r} - \mathbf{r}') \ ,$$

where $\mathbf{e}_q$ is a unit vector in arbitrary direction q. This cancels the integration and the sums over vector indices. We thus obtain

$$\left[\frac{\hbar^2}{m} [(\nabla_i \nabla_j \mathbf{u}_k) \bar{\mathcal{T}}_{kj} + \nabla_k (\nabla_j \mathbf{u}_k) \bar{\mathcal{T}}_{ji} + \nabla_j (\nabla_j \mathbf{u}_k) \bar{\mathcal{T}}_{ki} + \nabla_k \nabla_j (\nabla_i \nabla_j \mathbf{u}_k) \rho] \right.$$

$$\left. - \left[\mathbf{u}_k (\nabla_i \nabla_k v) \rho + (\nabla_i \mathbf{u}_k)(\nabla_k v) \rho + (\nabla_i \rho) \frac{\partial^2 \mathcal{U}}{\partial \rho^2} \mathbf{u}_k (\nabla_k \rho) \right] \right] = (\hbar \omega)^2 \rho \mathbf{u}_i \ . \quad (52)$$

Thus we see that in a restricted local RPA, a fairly overseeable set of fourth-order differential equations for $\mathbf{u}_i(\mathbf{r})$ can be derived. The equations resemble very much the hydrodynamical equations of da Providência and Holzwarth[6] or Krivine et al.[7] However, it turns out that such a differential equation is not the most efficient formulation for collective modes in a local RPA. A more stable approach is presented in Sec. III C.

Note that there is a choice in handling the variation $\delta \mathbf{u}$. The formally simpler procedure is to omit the constraint (51) and vary $\delta \mathbf{u}$ freely. In this way we have produced something more general than planned, namely an approximation which concentrates rather on a restriction to a "local" S of the form

$$S \equiv \tfrac{1}{2} \{ \mathbf{u}, \cdot \nabla \}$$

in terms of an arbitrary local vector function $\mathbf{u}(\mathbf{r})$. This also leads to Eq. (50). But one is, then, free of the restrictions (49) and (51), which means that one allows for rotational flow with $\nabla \times \mathbf{u} \neq 0$. One may come back to the "local-Q RPA" by requiring the condition of irrotational flow

$$\nabla \times \mathbf{u} = 0 \ , \quad (53)$$

i.e., that $\mathbf{u}(\mathbf{r})$ can be integrated to $Q(\mathbf{r})$ such that Eq. (49) holds. Thus we gain from the same variational equation (50) two versions of a local RPA, namely, (i) a "local-Q RPA" for which $Q \equiv Q(\mathbf{r})$, or (ii) a "local-S RPA" for which $S \equiv \tfrac{1}{2} \{ \mathbf{u}(\mathbf{r}), \cdot \nabla \}$, which both fulfill the same equation for $\mathbf{u}$. It is only the additional condition (53) for the "local-Q RPA" which can be carried as an additional Langrangian multiplier in Eq. (50). In the present paper, we restrict ourselves to the first version and call it henceforth just the "local RPA."

C. Momentum expansion

The local RPA looks simple as it gives a differential equation. However, this equation is of fourth order in the derivatives of Q. Such high-order equations can become quite critical numerically, and unwanted high-

Fourier components require special measures to ensure stability of the solution scheme. The results will, on the other hand, still not produce the exact RPA spectrum. Therefore we shall rather pursue here a global description which is particularly useful if most of a multipole strength is concentrated in one collective resonance. In that case, the simple sum-rule approach with the local operator

$$Q(\mathbf{r}) = r^L Y_{L0}(\theta) \quad (54)$$

gives already a very good first estimate. We improve it systematically here by an expansion in a few other moments of the same multipolarity. Thus we consider a basis of operators of the form

$$Q_\alpha^{(L)} = r^{p_\alpha} Y_{L0}(\theta) \ . \quad (55)$$

The upper index (L) is to indicate the multipolarity—it will be omitted in the following—and p_α is a real positive number. The optimal Q_n is then superposed as

$$Q_n = a_n^\alpha Q_\alpha \ , \quad (56)$$

and the variation is to be taken, of course, from the same subspace

$$\delta Q \in \{ Q_\alpha, \ \alpha = 1, \ldots, M \} \ . \quad (57)$$

The variational equation (44) leads then to a secular equation that determines a set of eigenenergies $\hbar \omega_n$ and superposition coefficients a_n^β:

$$[\mathcal{H}_{\alpha\beta} - (\hbar \omega_n)^2 \mathcal{B}_{\alpha\beta}] a_n^\beta = 0 \ . \quad (58)$$

Hereby

$$\mathcal{B}_{\alpha\beta} = \langle \Phi_0 | [Q_\alpha, [H, Q_\beta]] | \Phi_0 \rangle \ , \quad (59)$$

$$\mathcal{H}_{\alpha\beta} = \langle \Phi_0 | [[Q_\alpha, H], [H, [H, Q_\beta]]] | \Phi_0 \rangle \quad (60)$$

are the generalizations of the moments m_1 and m_3, respectively, so that the secular equation (58) is the generalization of the expression (28) for the energy E_3 to the

case of several coupled modes. In the notion of S scaling (see Appendix A), $\mathcal{H}$ is the stiffness tensor and $\mathcal{B}$ the mass tensor of the coupled modes. Since a_n^α need not be a unitary matrix, Eq. (58) leaves some freedom for them. We can choose as additional condition that they also diagonalize the mass tensor $\mathcal{B}$, such that the eigenmodes have orthogonal displacement fields $\tilde{u}_n$ and masses $\tilde{\mathcal{B}}_n$, i.e.,

$$\langle \Phi_0|[Q_n,[H,Q_m]]|\Phi_0\rangle = \frac{m}{\hbar^2} \int \tilde{u}_n \cdot \tilde{u}_m \rho(\mathbf{r})d^3r = \delta_{nm}\tilde{\mathcal{B}}_n .$$

(61)

Altogether, there remains the standard task of simultaneous diagonalization of the mass matrix $\mathcal{B}$ given in Eq. (59) and the stiffness matrix $\mathcal{H}$ in Eq. (60) by an appropriate choice of the coefficient matrix a_n^α.

Note that the RPA in restricted spaces of local Q always produces collective modes with irrotational flow, since $\nabla \times \mathbf{u}=0$ due to Eq. (49). However, one may also treat *rotational* hydrodynamics in the present formalism. To this end, a more general ansatz must be made at the level of the associated displacement fields:

$$S_\alpha = \tfrac{1}{2}\{\mathbf{u}_\alpha,\nabla\}, \quad \mathbf{u}_\alpha = r^{L-1+p}\mathbf{T}_{LL+\lambda M}, \quad \alpha = \{p,\lambda\}$$

(62)

where $\lambda = \pm 1$ and $\mathbf{T}_{LJM}$ are the vector spherical harmonics, see, e.g., Ref. 16. This, however, yields a considerably more complicated task; it should be attacked only if good reasons for the occurrence of rotational collective flow are found.

IV. EXAMPLE: DIPOLE PLASMONS IN METAL CLUSTERS

In order to illustrate the local RPA, sketched above, we present here some results for collective dipole excitations of the valence electrons in small metal clusters.[2-4] Some earlier results, using this method and employing semiclassical approximations, have been recently published by one of us.[13] These calculations are extended here to the purely microscopic level in the Kohn-Sham formalism.[17]

A. Energy functional and ground-state density

We employ the so-called jellium model[18-20] in which the charges of the ions (i.e., the atoms minus the valence electrons) are uniformly spread out over the volume of a sphere of radius $R_I = r_s Z^{1/3}$, where Z is the number of atoms, $r_s = [(4\pi/3)\rho_I]^{-1/3}$ is the Wigner-Seitz radius characterizing the metal, and ρ_I its density. Within the Kohn-Sham approximation[17] to the energy density formalism, we express the total energy of the cluster in terms of the local density $\rho(\mathbf{r})$ and the kinetic-energy density $\tau(\mathbf{r})$ of the valence electrons,

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2, \quad \tau(\mathbf{r}) = \sum_{i=1}^{N} |\nabla\varphi_i(\mathbf{r})|^2 ,$$

(63)

as

$$E[\rho] = \int \left[\frac{\hbar^2}{2m}\tau(\mathbf{r}) + \mathcal{E}_{xc}[\rho(\mathbf{r})] + \tfrac{1}{2}\rho(\mathbf{r})\left[e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r'\right] + V_I(\mathbf{r})\rho(\mathbf{r}) \right] d^3r + E_I .$$

(64)

Hereby $\mathcal{E}_{xc}[\rho]$ is the exchange and correlation energy density, and the third term is the Hartree Coulomb energy of the electrons; V_i and E_I are the potential and the total electrostatic energy, respectively, of the ionic jellium background. The density $\rho(\mathbf{r})$ is normalized to the number N of valence electrons:

$$\int \rho(\mathbf{r})d^3r = N .$$

(65)

Varying the energy (64) with respect to the single-particle wave functions $\varphi_i(\mathbf{r})$ leads to the usual Kohn-Sham (KS) equation

$$[\hat{T} + V_{tot}(\mathbf{r})]\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r}) .$$

(66)

$\hat{T}$ is the kinetic energy operator, and the local potential V_{tot} is a sum of three terms:

$$V_{tot}(\mathbf{r}) = V_{tot}[\rho(\mathbf{r})]$$
$$= V_{xc}[\rho(\mathbf{r})] + V_H[\rho(\mathbf{r})] + V_I(\mathbf{r}) ,$$

(67)

whereof the first is due to the exchange and correlation contributions:

$$V_{xc}[\rho(\mathbf{r})] = \frac{\delta}{\delta\rho(\mathbf{r})}\mathcal{E}_{xc}[\rho] ;$$

(68)

$V_H[\rho]$ is the Hartree potential of the electrons, given in the large parentheses in Eq. (64) above, and V_I is the jellium potential already mentioned.

We have solved Eq. (66) iteratively for spherical clusters on a finite mesh in $\mathbf{r}$ space using a standard code. For $\mathcal{E}_{xc}[\rho]$ we have used the local-density approximation (LDA) functional of Gunnarsson and Lundqvist.[21]

B. Pure electric multipole excitations

To discuss the collective excitations of the electrons in a cluster, such as the dipole vibrations seen experimentally by photoabsorption,[2,3] we shall now use the methods outlined in Sec. II and III above. In order to describe vibrations of multipolarity L, we shall first use the electric multipole operators in the long-wavelength limit (written in polar coordinates)

$$Q = Q_L(r,\theta) = r^L Y_{L0}(\theta) \quad (L \geq 1) .$$

(69)

These operators lead to divergence-free velocity fields, since $\Delta Q_L = 0$, thus describing pure surface oscillations during which the electron density is translated ($L=1$) or deformed ($L > 1$), but not compressed. For the operators (69), the moments m_3 and m_1 are relatively easy to evaluate and lead, for the Hamiltonian described by Eq. (64), to[13]

$$m_1(Q_L) = \frac{\hbar^2}{m} \frac{L}{2} \int r^{2L-2} \rho(r) d^3r ,$$ (70)

$$m_3(Q_L) = m_3^{\text{kin}} + m_3^{\text{Coul}} + m_3^{V_I} ,$$ (71)

with

$$m_3^{\text{kin}} = \frac{\hbar^2}{2m} \left[\frac{\hbar^2}{m} \right]^2 L(L-1)$$

$$\times \int r^{2L-4} \left[L\tau(r) + \frac{(L-2)}{2r^2} \lambda(r) \right] d^3r ,$$ (72)

$$m_3^{\text{Coul}} = - \left[\frac{\hbar^2}{m} \right]^2 \frac{L^2(L-1)}{(2L+1)} (4\pi e)^2$$

$$\times \int_0^\infty r^{2L-3} \rho(r) dr \int_0^r (r')^2 \rho(r') dr' ,$$ (73)

$$m_3^{V_I} = \left[\frac{\hbar^2}{m} \right]^2 \frac{L^2}{2(2L+1)}$$

$$\times \int V_I(r) r^{2L-4} [r^2 \rho''(r) + 2rL\rho'(r)] d^3r ,$$ (74)

where $\rho'(r), \rho''(r)$ are radial derivatives. Note that the exchange-correlation energy in the local-density approximation, like any part of the total energy which is only a *function* of $\rho(r)$, does not contribute to $m_3(Q_L)$ (see also Ref. 5). In the kinetic energy term (72), $\lambda(r)$ is an angular momentum density defined in terms of the single-particle wave functions φ_i by

$$\lambda(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2 l_i(l_i+1) ,$$ (75)

where l_i is the angular momentum quantum number of the state i.

As shown in Ref. 13, the RPA energy $E_3(Q_L)$, Eq. (28), tends in the limit of a large spherical cluster to the classical Mie energy[22] of the surface plasmon:

$$\lim_{R \to \infty} E_3(Q_L) = \hbar\omega_L^{\text{Mie}} = \sqrt{L/(2L+1)} \hbar\omega_{\text{pl}} \quad (L \geq 1) ,$$ (76)

where ω_{pl} is the bulk plasma frequency:

$$\omega_{\text{pl}} = \left[\frac{3e^2}{mr_s^3} \right]^{1/2} = \left[\frac{4\pi e^2 \rho_I}{m} \right]^{1/2} .$$ (77)

Similarly, one finds[13] that for an *arbitrary but local* operator $Q_0(r)$ with multipolarity $L = 0$, the energy E_3 goes to the bulk plasmon energy in the classical limit:

$$\lim_{R \to \infty} E_3(Q_0) = \hbar\omega_{\text{pl}} \quad (L = 0) .$$ (78)

C. Momentum expansion

In finite clusters we have to expect a coupling of surface and volume plasmons for all multipolarities $L > 0$, as pointed out by Ekardt[23] in the dipole case. In order to study such a coupling in our present approach, we introduce a set of trial operators

$$Q_\alpha^{(L)} = r^{p_\alpha} Y_{L0}(\theta) ,$$ (79)

with p_α being a positive real number. For $p_\alpha \neq L$, we have $\Delta Q_\alpha^{(L)} \neq 0$ and this operator will describe modes which involve local compression of the electrons. We therefore shall solve the secular equation (58), coupling the modes obtained with (79) using different values of p_α. This is just the momentum expansion of the local RPA which was discussed extensively in Sec. III C and which leads us to a spectrum of eigenmodes with energies $\hbar\omega_n$ and orthonormalized velocity fields $\tilde{u}_n$ according to Eq. (61). The algebraic evaluation of the matrices Eqs. (59) and (60) with our trial operators (79) is rather cumbersome, in particular for the kinetic-energy contributions. We give the explicit formulas in Appendix B.

For a given (external) excitation operator Q_{ex} we then calculate sum rules m_k by[13,14]

$$m_k(Q_{\text{ex}}) = \sum_{n=1}^M (\hbar\omega_n)^k |\langle n|Q_{\text{ex}}|0\rangle|^2 ,$$ (80)

where the transition probabilities are given by

$$|\langle n|Q_{\text{ex}}|0\rangle|^2 = \frac{\hbar}{2\omega_n \tilde{\mathcal{B}}_n} \left| \int Q_{\text{ex}}(\mathbf{r}) \delta\rho_n d^3r \right|^2 ;$$ (81)

$\tilde{\mathcal{B}}_n$ is the mass of the nth normal mode appearing in Eq. (61), and $\delta\rho_n$ is the transition density from the ground state to the one-phonon state with energy $\hbar\omega_n$:

$$\delta\rho_n = -\nabla\cdot(\rho\tilde{u}_n) = \frac{\hbar^2}{m} \nabla\cdot(\rho\nabla Q_n) .$$ (82)

Practically, this amounts to expanding the operator Q_{ex} in terms of the eigenmodes $\tilde{u}_n$. Thus, by construction, Eq. (80) gives the correct RPA sum rules $m_1(Q_{\text{ex}})$ and $m_3(Q_{\text{ex}})$ for local operators $Q_{\text{ex}}(\mathbf{r})$ whose gradients lie in the space spanned by the $\tilde{u}_n$; meaning that the one-phonon eigenstates of Eq. (58) exhaust these two sum rules exactly.[14] This is, in particular, true for the electric multipole operators Q_L, Eq. (69), for which the moments m_1 and m_3 are directly given by Eqs. (70) and (71) in terms of the ground-state densities ρ, τ, and λ. [The equality of these values with the ones obtained on the right-hand side of Eq. (80) can therefore be used as a test of the numerical precision of the calculations.]

Evaluating furthermore the moments m_0 and m_2 from Eq. (80), we obtain our local RPA estimates for the centroid $\bar{E}$ and the variance σ, defined in Eq. (26), of the strength function. From the moment m_{-1} we get finally the static polarizability α via Eq. (23).

D. Surface and volume plasmons in the classical limit

Before giving numerical results for microscopic clusters, we shall briefly summarize the results obtained[13] in the classical limit of macroscopic metal spheres. For a very large cluster, the diffuseness of the electron density can be ignored, so that we can take ρ to be a step function: $\rho(r) = \rho_{0I}\Theta(R_I - r)$. Furthermore, the kinetic and exchange-correlation energies vanish as $N^{-2/3}$ with respect to the leading Coulomb contributions. The matrices (59) and (60) can then be evaluated analytically.[13] Solving the secular equations (58) for a given set of M

different trial operators (79) for a fixed multipolarity $L > 0$ leads to the following result: there are always $M - 1$ degenerate eigenvalues $\omega = \omega_{pl}$, independently of Q_L^p, and one nondegenerate eigenvalue $\omega = \omega_L$ which is close to or, if one of the p_i equals L, identical to the classical Mie frequency[22] of the surface plasmon: $\omega_L = \omega_L^{Mie}$, Eq. (76).

Thus in classical metal spheres there exist for each multipolarity $L > 0$ a *surface plasmon* with the Mie frequency and a (infinitely degenerate) *volume plasmon* with the bulk plasma frequency. It should be noted that in this classical limit, the surface plasmon takes up all of the strength of the multipole operator Q_L, and the volume plasmons are decoupled. The fact that all volume plasmons are degenerate in this limit means that the energies E_3 of these solutions do not depend on the radial form of the operator Q. This in itself is not surprising since this limit is *defined* as the one where the electron density is constant over the whole volume of the cluster.

In the case of multipolarity $L = 0$, there are *always* M degenerate eigenvalues with the bulk plasma frequency ω_{pl} (77), which follows immediately from (78).

In real finite clusters, quantum and size effects will change these results. In fact, the kinetic energy of the electrons, their exchange and correlation effects, and the finite diffusivity of their density $\rho(r)$ will lift the degeneracy of the volume plasmons and give them a finite multipole strength. This leads to a fragmentation (Landau damping) of the surface plasmon, as observed in the calculations of Ekardt[23] and also in some recent RPA calculations.[24]

E. Results for finite spherical clusters

In our numerical calculations we have solved the KS equations (66), then evaluated the mass and stiffness tensors (59) and (60) using the microscopic ground-state densities $\rho(r)$, $\tau(r)$, and $\lambda(r)$ (see Appendix B for the detailed formulas), and finally solved the secular equation (58) for finite spherical clusters. We restrict ourselves here to dipole oscillations ($L = 1$), as they have recently been observed experimentally by photoabsorption on small alkali clusters.[2,3] For most of the examples shown here we chose sodium clusters, using $r_s = 3.96$ a.u.

We first discuss the convergence of our expansion method with respect to the number M of coupled modes and the powers p_α of the trial operators (79) used to obtain the eigenmode spectrum. Figure 1 shows the convergence of the lowest eigenvalues $\hbar\omega_1$, the centroid $\bar{E}$, and the polarizability α of the Na_8 cluster as functions of the number M of coupled dipole modes ($L = 1$). The various symbols correspond to different selections of powers p_α (see the figure caption). We see that the convergence as a function of M is excellent. Also, the results are quite independent of the particular choice of the p_α, as long as powers in the range $8 < p_\alpha < 12$ are involved. For too close values of the powers ($\Delta p_\alpha \leq 1$), the basis becomes overcomplete and no good plateau can be found. As a "rule of thumb," a basis of five expansion operators (79) with $p_\alpha = (1,4,7,10,13)$ gives unique and stable results up

to three digits for all the quantities discussed here, including the variances σ, for all cluster sizes. Similar results are obtained for the two or three next higher eigenvalues $\hbar\omega_n$, as long as their contribution to the m_1 sum rule is significant ($> 1\% - 2\%$).

We now compare the converged results to those of recent full RPA calculations by Yannouleas *et al.*[24] using the same energy functional (64). [Strictly speaking, the calculations in Ref. 24 were not done with the exact Kohn-Sham potentials, but with their averages obtained in semiclassical extended Thomas-Fermi (ETF) density variational calculations.[13] However, the single-particle wave functions and spectra obtained from those average ETF potentials are so close to those of the microscopically iterated KS potentials, that the differences in all the quantities compared below are well below 1%.] In the upper part of Fig. 2, we show the full RPA dipole spectrum $\hbar\omega_n$ of Na_8; in the lower part, the spectrum obtained in our present local RPA approximation is displayed. In both cases, the height of the vertical lines gives the percentage contribution of each state to the dipole sum rule, $m_1(Q_1) = (\hbar^2/2m)e^2N$. Shown are all
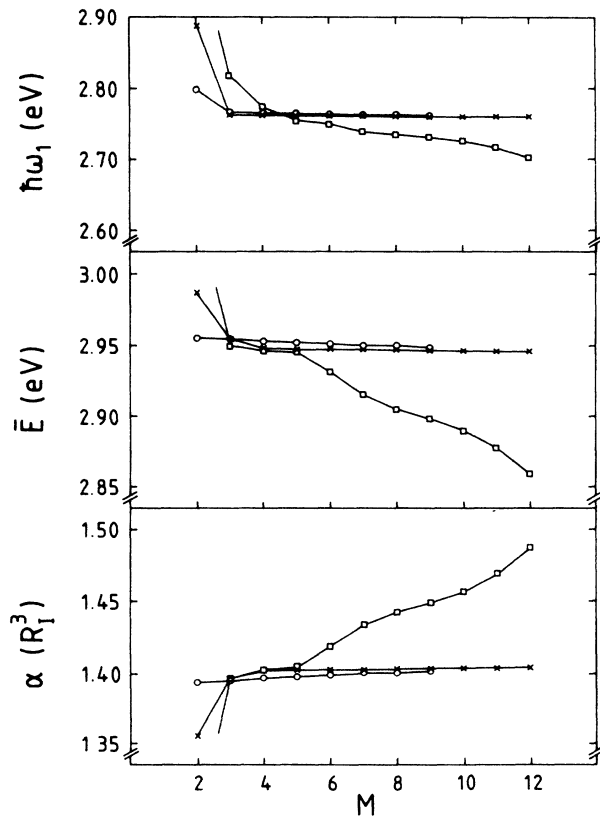

FIG. 1. Collective dipole properties of the Na_8 cluster, obtained in the present local RPA approach. Top: lowest eigenenergy $\hbar\omega_1$; middle: centroid $\bar{E}$; bottom: static polarizability α. The results are plotted vs the number M of coupled modes. The powers p_α were chosen as follows. Boxes: $p_\alpha = (1,2,3,\ldots,M)$; crosses: $p_\alpha = (1,3,5,\ldots,2M-1)$; circles: $p_\alpha = (1,4,7,\ldots,3M-2)$.
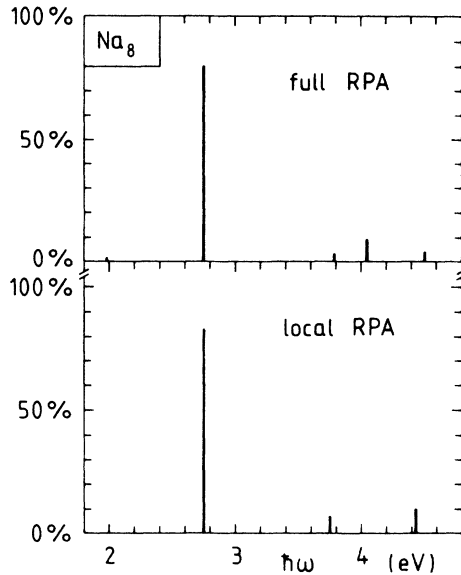
FIG. 2. Collective dipole spectrum of Na_8. Above: full RPA results (Ref. 24); below: present local RPA results. The height of the vertical lines gives the percentage of the corresponding states to the dipole sum rule.

states that contribute 1% or more to this sum rule. The same is presented in Fig. 3 for Na_{20}. In the case of Na_8, the agreement is almost quantitative for the most collective (i.e., the lowest) state. For the neutral Na_{20}, the full RPA dipole strength shows a splitting into mainly two collective peaks, as already discussed in Ref. 24. Our local RPA does not reproduce this splitting; we get mainly one peak (with 78% of m_1). We mention in passing that
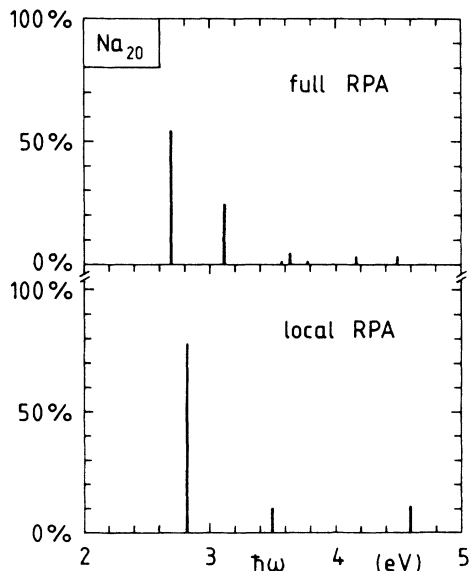
FIG. 3. Same as Fig. 2, but for Na_{20}.

the amount of splitting found in the full RPA calculation[24] is extremely sensitive to the details of the exchange-correlation energy functional $\mathscr{E}_{xc}[\rho]$ employed. The experimental verification of such structures would therefore be a challenge for further tests and improvements of this energy density functional.

The states above 3.0–3.5 eV seen in the above RPA spectra should not be given too much quantitative significance. Physically, they represent the (fragmented) volume plasmon, which is only weakly coupled to the surface plasmon. However, since they lie in the continuum, their position is rather crucially dependent on the particular way in which the high-lying particle states have been treated numerically in the RPA calculation. They were obtained in Ref. 24 by discretizing the continuum in a harmonic-oscillator basis. In the local RPA calculation, this problem does not exist, because here one only needs to know the occupied ground-state single-particle wave functions for evaluating all the ingredients to the secular equation (58). It is therefore gratifying that the average properties derived from the various moments of the spectra obtained in the two approaches agree very well. We show in Table I the energies E_3, E_1, Eq. (25), the centroids $\bar{E}$ and variances σ, Eq. (26), and the static polarizabilities α, Eq. (23), of Na_8 and Na_{20}, obtained in the two calculations. The differences are slightly larger in the case of Na_{20}, where the local RPA does not reproduce the splitting of the collective peak, but the overall degree of agreement is very satisfactory.

It might be interesting also to compare our polarizabilities α to those of the time-dependent LDA (TDLDA) calculations by Beck and Ekardt.[20,23] The latter are indicated in Fig. 4 by the square boxes, whereas our present results are interpolated by the solid line. The agreement is quantitative, although our way of calculating α is quite different from that of Refs. 20 and 23. There, an explicit linear-response calculation with an external electric di-
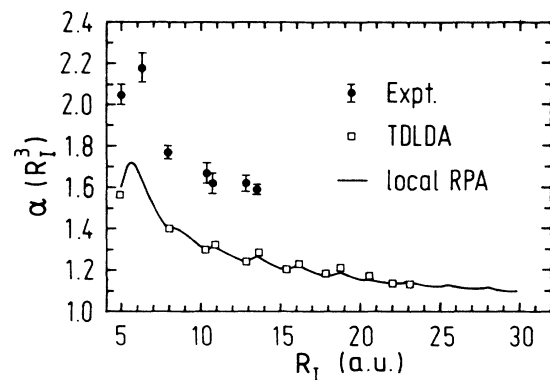
FIG. 4. Static dipole polarizabilities α (in classical units R_I^3) of spherical Na clusters, obtained with $\alpha = 2m_{-1}$ from the sum rule m_{-1} with the help of our local RPA spectrum, vs cluster (jellium) radius R_I. The boxes represent the TDLDA results of Refs. 20 and 23 (which agree with each other within the size of the boxes). The dots with error bars show the experimental results of Knight et al. (Ref. 25).

TABLE I. Energies E_3, E_1, centroids $\bar{E}$, and variances σ of the collective dipole spectrum, and static electric dipole polarizabilities α, for the neutral clusters Na_8 and Na_{20}, obtained both in full RPA calculations (Ref. 24) and in the present approach. (Here the value $r_s = 4.0$ a.u. was used).

| | Na_8 | | Na_{20} | |
	Full RPA	Local RPA	Full RPA	Local RPA
E_3 (eV)	3.08	3.08	3.14	3.15
$\bar{E}$ (eV)	2.91	2.91	2.98	3.00
E_1 (eV)	2.87	2.88	2.93	2.97
σ (eV)	0.54	0.52	0.55	0.51
α (R_I^3)	1.40	1.39	1.35	1.31

pole field was used. The connection between the two ways of calculation is given by the "dielectric theorem," Eq. (23). To the extent that the calculations of Refs. 20 and 23 represent a Kohn-Sham-LDA approximation to the constrained Hartree-Fock (HF) problem, Eq. (24), their polarizabilities can be identified with $2m_{-1}$ obtained from a RPA spectrum. The excellent numerical agreement of our values of α with theirs confirms this indeed. Note that, once the formalism of the present paper and the expressions in Appendix B are at our disposal, our way of calculating the static polarizabilities is much easier and faster than that of Refs. 20 and 23, because only the knowledge of the *ground-state wave functions* is required.

We finally compare our results to the experimental ones. The peak of the resonance curve seen[2] in Na_8 lies at about 2.5 eV. Our result for the most collective eigenstate (82% of m_1, see Fig. 2) is 2.75 eV, thus not sufficiently red shifted with respect to the classical Mie dipole plasmon which lies at 3.45 eV. This lack of red shift has the same origin as the deficiency of the static polarizabilities[13,20,23,25] (see Fig. 4) and will, hopefully, be removed in a better treatment of the Coulomb exchange.[26] Note, however, that the *relative* variation of the experimental α with R_I is quite well reproduced by our calculations shown in Fig. 4, particularly also the drop for the lightest cluster with $Z = 2$ ($R_I = 4.99$ a.u.).

The situation for the dipole peak is very similar in the Na_{20} cluster.[2,24] In *ionized* clusters, the electrons are deeper bound and the dominant dipole peaks become even more collective (see also Ref. 24). To illustrate this, we show in Table II the results obtained in our present

TABLE II. Dipole plasmons in the charged potassium clusters K_9^+ and K_{21}^+. The first column gives the experimental peak energies (in eV) measured by Bréchignac et al. (Ref. 3). The second column gives the lowest eigenmode energy $\hbar\omega_1$ (in eV) of the collective dipole spectrum obtained in the local RPA and, in parentheses, its contribution to the dipole sum rule. The value $r_s = 4.86$ a.u. was used for potassium.

	Expt.	Local RPA $(\%m_1)$
K_9^+	1.93	2.31 (94.9)
K_{21}^+	1.98	2.33 (96.9)

method for two singly ionized potassium clusters, whose dipole plasmons have recently been observed experimentally.[3] We see that the lowest collective dipole state $\hbar\omega_1$ here exhausts more than 90% of the dipole sum rule. The lack of red shift is similar to that obtained for the Na clusters.

We mentioned in Sec. IV D that in the classical limit of a large metallic sphere, the RPA dipole response just yields the classical Mie surface plasmon and the bulk plasmon, the vanishing coupling of surface to volume plasmon reflecting itself in a vanishing variance σ of the spectrum. This is illustrated in Fig. 5 where we show our results obtained for the energy centroid $\bar{E}$, the lowest eigenenergy $\hbar\omega_1$, and the variance σ of Na clusters, plotted versus the cluster radius R_I. The classical (Mie) surface-plasmon energy $\hbar\omega_1^{Mie}$ is shown as the horizontal line. In the earlier semiclassical calculations of Ref. 13, it was seen that this limit is reached by $\bar{E}$ and $\hbar\omega_1$ within one part per thousand for Na clusters with radii larger than 80 a.u. corresponding to $N > 8000$. It was also shown in Ref. 13 that the variance σ asymptotically vanishes like $Z^{-1/6}$, i.e., like $1/(R_I)^{1/2}$; this slow decrease can be observed in Fig. 5.

In both Figs. 4 and 5, we see that the shell effects play a relatively small role and tend to disappear with increasing cluster radius. Thus, for large clusters in the mesoscopic domain $N > 1000$, all the collective properties discussed here can be well described in semiclassical density variational calculations[13] where one does not iterate microscopic single-particle wave functions via the Kohn-Sham equations, but varies only the electronic densities $\rho(r)$ employing the ETF gradient-expanded functional $\tau[\rho]$ for the kinetic-energy density, and afterwards evaluates collective mass and stiffness tensors in terms of the semiclassical ground-state densities. Such calculations yield,[13] indeed, the average parts of the results shown in Figs. 4 and 5 above, the eigenmode spectra of the coupled-modes problem being very close to those depicted in Figs. 2 and 3. But ETF variational calculations are much faster than the microscopic KS calculations and provide thus a very efficient tool for investigating large clusters (up to $N = 10^6$ or more), where microscopic methods become numerically too time consuming. Even for smaller clusters they provide a very useful starting point for the KS procedure.
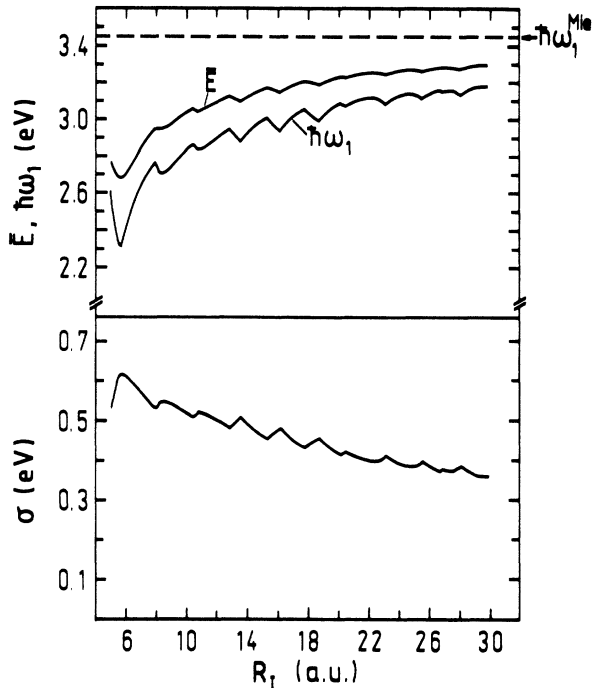
FIG. 5. Centroid $\bar{E}$ (top solid line), lowest eigenenergy $\hbar\omega_1$ (middle solid line), and variance σ (bottom solid line) of the collective dipole spectrum obtained in local RPA for Na clusters ($r_s = 3.96$ a.u.), vs cluster (jellium) radius R_I. The horizontal dashed line indicates the classical (Mie) surface-plasmon energy.

V. SUMMARY AND OUTLOOK

In order to obtain a flexible starting point for collective approaches, we have reformulated the RPA algebra in a so-called Q-P description in terms of coordinatelike operators Q and momentumlike operators P. We have shown that one can recover the full RPA equations by varying the RPA energy $\hbar\omega(Q)$ with respect to the operator Q. This, in turn, gives us a variational principle at hand for approximations to RPA in restricted spaces for the choice of Q. We want to point out that we take as the starting point a RPA which is built self-consistently on top of a full microscopic Hartree-Fock (or Kohn-Sham) calculation using the same Hamiltonian. Unlike in most earlier approaches, this feature is retained for all choices of Q (or P). Approximations are done only at the RPA level.

As a most obvious application, we have investigated a local RPA where Q is taken from the space of local one-body operators, $Q = Q(\mathbf{r})$. From varying $\hbar\omega(Q)$, one can derive a differential equation for $Q(\mathbf{r})$ which resembles very much the differential equations of the hydrodynamical (or fluid dynamical) approaches to collective motion in quantum many-body systems. However, this is a differential equation of fifth order and thus numerically quite inconvenient to handle. We therefore prefer an integral approach where we expand the radial part of $Q(\mathbf{r})$ in powers of r and determine the expansion coefficients by

a secular equation which results from variation with respect to the expansion coefficients. This treatment is numerically simpler and more stable; it automatically yields a (restricted) spectrum of eigenmodes and thus does not require the orthogonalization procedure necessary in solving the differential equation for $Q(\mathbf{r})$. Our method is also more realistic than earlier fluid dynamical approaches (see, e.g., Refs. 6 and 27), in that it makes use of fully self-consistent and microscopic densities.

We have tested and exemplified the local RPA for the collective electronic dynamics of metallic clusters. We find, indeed, that the method is numerically very efficient and stable. Comparison with a full RPA calculation shows that the local approach works very well in our example. The average features of the resonances are always well reproduced. The full RPA shows sometimes a splitting of the strength in the resonance region. It remains to be seen whether this feature can be described in an extended collective picture or whether this is a typical particle-hole property.

The local RPA from varying $Q(\mathbf{r})$ represents a hydrodynamics with *irrotational* collective flow. We have shown that one can extend the approach easily to cover also *rotational* flow. One knows that level splitting leads to curls in the flow pattern. It is interesting to see whether one can conclude the reverse way, namely, that the freedom to have rotational flow leads to the observed level splitting already on this purely collective picture. This will be the next step in the future development of our model.

Finally we want to note that the collective dynamics of metallic clusters has many similarities with the collective dynamics of nuclei. Thus the methods explained in this paper apply also to that case. Investigations of *nuclear giant resonances* have, indeed, been performed in local RPA using two coupled modes.[28,29,14] More refined extensions are presently under way.[30]

APPENDIX A: SCALING TRANSFORMATION AND SCALES FOR THE COLLECTIVE VARIABLE

The RPA equations (34) and (35) suggest an interpretation of $\langle \Phi_0 | [Q,[H,Q]] | \Phi_0 \rangle$ as the inverse mass $\mathcal{B}$ and $\langle \Phi_0 | [P,[H,P]] | \Phi_0 \rangle$ as the spring constant $\mathcal{C}$ of the RPA mode. On the other hand, one finds in some publications, e.g., Ref. 5, a different interpretation where $\mathcal{B}$ is directly the mass and the spring constant is rather $\langle \Phi_0 | [[Q,H],[H,[H,Q]]] | \Phi_0 \rangle = \mathcal{H}$. Both points of view are right. There is indeed some freedom of scale in assigning a collective coordinate to a mode. We will explain in this appendix the implications of the two choices.

First we discuss the Q scaling which is connected to the RPA equations (34) and (35). For the interpretation, we recur to the generator coordinate method[31] and construct a static deformation path by

$$|\Phi_q\rangle = e^{-iqP}|\Phi_0\rangle , \quad \text{(A1)}$$

where P is the momentum conjugate to Q. In particular in the local RPA, we choose

$$P = i[H,Q]/\mathcal{B} , \quad \text{(A2)}$$

where the division with $\mathcal{B} = \langle\Phi_0|[Q,[H,Q]]|\Phi_0\rangle$ serves to adjust the conjugation relation $\langle\Phi_0|[Q,P]|\Phi_0\rangle = i$. The q is the collective variable which labels the deformation. It is scaled such that in first order of q

$$\langle\Phi_q|Q|\Phi_q\rangle = q . \quad \text{(A3)}$$

It, so to speak, "measures" the Q operator. However, the RPA is a theory of dynamics and we need to extend the path (A1) to a dynamic path[31]

$$|\Phi_{qp}\rangle = e^{ipQ}e^{-iqP}|\Phi_0\rangle , \quad \text{(A4)}$$

from which we can construct a classical Hamiltonian

$$\mathcal{H} = \langle\Phi_{qp}|H|\Phi_{qp}\rangle , \quad \text{(A5)}$$

which in the small-amplitude limit becomes an oscillator Hamiltonian

$$\mathcal{H} = \tfrac{1}{2}\mathcal{B}p^2 + \tfrac{1}{2}\mathcal{C}q^2 ,$$

$$\mathcal{B} = \frac{\partial^2}{\partial p^2}\mathcal{H} = \langle\Phi_0|[Q,[H,Q]]|\Phi_0\rangle , \quad \text{(A6)}$$

$$\mathcal{C} = \frac{\partial^2}{\partial q^2}\mathcal{H} = \langle\Phi_0|[P,[H,P]]|\Phi_0\rangle .$$

The last equation makes the interpretation of $\mathcal{B}$ as inverse collective inertia and of $\mathcal{C}$ as spring constant obvious. Note that this interpretation is related to the choice of the Q scaling (A3).

An alternative viewpoint is taken in the S scaling. There one starts from the scaling operator

$$S = [H,Q] \quad \text{(A7)}$$

and generates the static deformation path by

$$|\tilde{\Phi}_\beta\rangle = e^{-\beta S}|\Phi_0\rangle . \quad \text{(A8)}$$

The S-scaling path as a whole, $\{|\tilde{\Phi}_\beta\rangle\}$, is identical to the Q-scaling path $\{|\Phi_q\rangle\}$. But the static deformation is labeled differently. The relation between the two labelings is

$$|\tilde{\Phi}_\beta\rangle = |\Phi_q\rangle \quad \text{where } q = -\mathcal{B}\beta . \quad \text{(A9)}$$

The first step has been taken simpler in the S scaling. The work comes now in constructing the momentum conjugate. The momentum label γ, conjugate to β, is related to the momentum label p by $\gamma = \mathcal{B}p$. Thus we construct the according dynamic path by

$$|\tilde{\Phi}_{\beta\gamma}\rangle = e^{-i\gamma Q/\mathcal{B}}e^{-\beta S}|\Phi_0\rangle , \quad \text{(A10)}$$

from which we can construct the classical Hamiltonian

$$\tilde{\mathcal{H}} = \langle\tilde{\Phi}_{\beta\gamma}|H|\tilde{\Phi}_{\beta\gamma}\rangle , \quad \text{(A11)}$$

which becomes in the small-amplitude limit an oscillator Hamiltonian:

$$\tilde{\mathcal{H}} = \frac{1}{2\mathcal{B}}\gamma^2 + \tfrac{1}{2}\tilde{\mathcal{K}}\beta^2 ,$$

$$\mathcal{B} = \left[\frac{\partial^2}{\partial\gamma^2}\tilde{\mathcal{H}}\right]^{-1} = \langle\Phi_0|[Q,[H,Q]]|\Phi_0\rangle = 2m_1(Q) ,$$

$$\text{(A12)}$$

$$\tilde{\mathcal{K}} = \frac{\partial^2}{\partial\beta^2}\tilde{\mathcal{H}} = \langle\Phi_0|[[Q,H],[H,[H,Q]]]|\Phi_0\rangle = 2m_3(Q) .$$

Thus in the S scaling we find that $\mathcal{B}$ is directly the collective inertia, but this goes in connection with an accordingly rescaled spring constant $\tilde{\mathcal{K}}$.

For local operators $Q(\mathbf{r})$ which commute with the potential energy V in the total Hamiltonian $H = T + V$, the S-scaling transformation (A8) and the moments m_1, m_3 have a transparent physical meaning. That $2m_3 = \tilde{\mathcal{K}}$ is a spring constant, obtained from the scaled ground-state energy $\tilde{\mathcal{H}}$, is directly seen from Eq. (A12) above. That $\mathcal{B}$ is a hydrodynamical mass parameter, can be seen in the following way. We write

$$S = [H,Q] = [T,Q] = \tfrac{1}{2}\{\mathbf{u},\cdot\nabla\} \equiv \tfrac{1}{2}(\nabla\cdot\mathbf{u}) + \mathbf{u}\cdot\nabla , \quad \text{(A13)}$$

where $\mathbf{u}$ is a displacement field corresponding to the velocity potential $Q(\mathbf{r})$:

$$\mathbf{u}(\mathbf{r}) = -\frac{\hbar^2}{m}\nabla Q(\mathbf{r}) . \quad \text{(A14)}$$

Indeed, taking $\beta(t)$ as a collective variable and defining the velocity field

$$\mathbf{v}(\mathbf{r},t) = \dot{\beta}(t)\mathbf{u}(\mathbf{r}) , \quad \text{(A15)}$$

it is easy to see,[5,14] using the obvious operator identity

$$-\frac{\partial}{\partial\beta} = S , \quad \text{(A16)}$$

that $\mathbf{v}$ and the scaled ground-state density $\rho_\beta(\mathbf{r})$ fulfill the continuity equation

$$\frac{\partial}{\partial t}\rho_\beta + \nabla\cdot(\rho_\beta\mathbf{v}) = 0 \quad \text{(A17)}$$

and that

$$\mathcal{B} = \frac{m}{\hbar^2}\int \mathbf{u}^2(\mathbf{r})\rho(\mathbf{r})d^3r . \quad \text{(A18)}$$

APPENDIX B: EVALUATION OF THE MASS AND STIFFNESS TENSORS FOR THE TRIAL OPERATORS OF SEC. IV C

We evaluate here the commutators in Eqs. (59) and (60). To simplify the notation, let us redefine the trial operators (79) as

$$Q_L^p = r^p Y_{L0}(\theta) \quad (L \geq 0) \tag{B1}$$

and replace the pairs of indices (α, β) in Sec. III C by (p, p'). Generalizing Eqs. (A13)–(A18) of the S scaling concept discussed in Appendix A above to the multidimensional case, we define the scaling operator S_L^p by

$$S_L^p = [H, Q_L^p] = [T, Q_L^p] = \tfrac{1}{2}(\nabla \cdot \mathbf{u}_L^p) + \mathbf{u}_L^p \cdot \nabla , \tag{B2}$$

where $\mathbf{u}_L^p$ is the displacement field corresponding to the operator Q_L^p:

$$\mathbf{u}_L^p(\mathbf{r}) = -\frac{\hbar^2}{m} \nabla Q_L^p(\mathbf{r}) . \tag{B3}$$

The mass tensor defined in Eq. (59) is easily shown, by partial integration, to be

$$\mathcal{B}_{pp'} = \frac{m}{\hbar^2} \int \mathbf{u}_L^p(\mathbf{r}) \cdot \mathbf{u}_L^{p'}(\mathbf{r}) \rho(\mathbf{r}) d^3 r \tag{B4}$$

and thus, indeed, is a classical hydrodynamical mass tensor. For spherical densities $\rho(r)$ we find after the angular integrations

$$\mathcal{B}_{pp'} = \left[\frac{\hbar^2}{m}\right] \frac{pp' + L(L+1)}{(2L+1)} (4\pi) \int_0^\infty r^{p+p'} \rho(r) dr . \tag{B5}$$

The stiffness tensor defined in Eq. (60) can be rewritten as

$$
\begin{aligned}
\mathcal{H}_{pp'} &= \langle \Phi_0 | [S_L^p, [S_L^{p'}, H]] | \Phi_0 \rangle \\
&\equiv \frac{d^2}{d\beta d\beta'} [\langle \Phi_0 | e^{\beta S_L^p} H e^{-\beta' S_L^{p'}} | \Phi_0 \rangle]_{\beta=\beta'=0} \\
&= \frac{d^2}{d\beta d\beta'} [\langle \beta | H | \beta' \rangle]_{\beta=\beta'=0} ,
\end{aligned} \tag{B6}
$$

where

$$|\beta\rangle = e^{-\beta S_L^p} |\Phi_0\rangle \tag{B7}$$

is the scaled ground state. The latter equality on the right-hand side of Eq. (B6) facilitates the calculations appreciably. The results can be given in the following way. We write

$$\mathcal{H}_{pp'} = \mathcal{H}_{pp'}^{\text{kin}} + \mathcal{H}_{pp'}^{\text{xc}} + \mathcal{H}_{pp'}^{\text{Coul}} + \mathcal{H}_{pp'}^{V_I} . \tag{B8}$$

Note that even though S_L^p and $S_L^{p'}$ do not commute in general, $\mathcal{H}_{pp'}$ in Eq. (B6) would be symmetric if $|\Phi_0\rangle$ were an eigenstate of H. This is, however, not exactly true in the KS approximation. It is therefore reasonable to symmetrize the single terms in (B8).

The kinetic-energy contribution $\mathcal{H}_{pp'}^{\text{kin}}$ for $p, p' \neq L$ with $L > 1$ involves complicated angular momentum algebra and is very cumbersome to evaluate in general. Since we are concerned with the dipole case $(L = 1)$ in this paper, we have only calculated this case analytically here. The results for $L = 1$ reads, for spherical densities, after symmetrization,

$$
\mathcal{H}_{pp'}^{\text{kin}} = \left[\frac{\hbar^2}{m}\right]^3 \int r^{p+p'-6} [a_{p,p'} r^2 \tau(r) + b_{p,p'} \lambda(r) + c_{p,p'} \rho(r)] d^3 r , \tag{B9}
$$

where

$$a_{p,p'} = \tfrac{1}{6}(pp' + 2)[4pp' - p^2 - (p')^2 - p - p'] ,$$

$$b_{p,p'} = -\tfrac{1}{6}\{pp'[4pp' - p^2 - (p')^2 - 6] - 2[p^2 + (p')^2] + 12(p + p') - 16\} ,$$

$$
\begin{aligned}
c_{p,p'} = -\tfrac{1}{6}\{&[p(p+1) - 2][p'(p'+1) - 2][pp' - 2(p+p') + 6] \\
&+ \tfrac{1}{2}[(p'-1)(p'+2)(p-1)(p'-3)(pp' - 2p + 6) + (p \leftrightarrow p')] \\
&- \tfrac{1}{4}[p(p-1)(p+2)(p-3)(pp' - 4p' + 2) + (p \leftrightarrow p')]\} .
\end{aligned}
$$

The remaining contributions to Eq. (B8) have already been given in Ref. 13; we repeat them here for completeness, correcting a misprint in Eq. (A10) of Ref. 13 [note the minus sign in front of the first term in the brackets of Eq. (B12) below]. The exchange-correlation contribution has been evaluated in the local-density approximation. It is obtained using the following formula which holds for any part of the energy that is just a spatial integral over a *function* f of the density $\rho(r)$. Let E_f be given by

$$E_f = E_f[\rho] = \int f(\rho(r)) d^3 r . \tag{B10}$$

Then the symmetrized contribution of E_f to (B6) is found to be

$$
\begin{aligned}
\mathcal{H}_{pp'}^f = \frac{1}{2} \left[\frac{\hbar^2}{m}\right]^2 \frac{4\pi}{(2L+1)} \int_0^\infty r^{p+p'-2} \Bigg[&(p + p' - 1)\{p[p'(p'+1) - \hat{L}^2] + p'[p(p+1) - \hat{L}^2]\} \\
&\times \left[f(\rho) - \rho \frac{df(\rho)}{d\rho}\right] + 2[p(p+1) - \hat{L}^2][p'(p'+1) - \hat{L}^2]\rho^2 \frac{d^2 f(\rho)}{d\rho^2} \Bigg] dr .
\end{aligned}
$$

Hereby we use the notation

$$\hat{L}^2 = L(L+1) . \tag{B11}$$

The symmetrized Hartree-Coulomb contribution to $\mathcal{H}_{pp'}$ is

$$\mathcal{H}_{pp'}^{\text{Coul}} = \left[\frac{\hbar^2}{m}\right]^2 \frac{(4\pi e)^2}{(2L+1)}$$

$$\times \int_0^\infty \rho(r) \left[-\frac{1}{2}[(p+p')\hat{L}^2 + pp'(p+p'-6)]r^{p+p'-3} \int_0^r r'^2 \rho(r')dr' \right.$$

$$+ \frac{\hat{L}^2}{(2L+1)} \left[(L-p')(p+L+1)r^{p'-L-1} \int_0^r r'^{L+p}\rho(r')dr' \right.$$

$$\left. \left. +(L-p)(p'+L+1)r^{p-L-1} \int_0^r r'^{L+p'}\rho(r')dr' \right] \right] dr .$$

$$(B12)$$

The contribution from any external spherical potential $V_I(r)$, finally, is

$$\mathcal{H}_{pp'}^{V_I} = \frac{1}{2} \left[\frac{\hbar^2}{m}\right]^2 \frac{4\pi}{(2L+1)} \int_0^\infty V_I(r)r^{p+p'-2}\{(p+p'-1)[(p+p'+2)pp' - (p+p')\hat{L}^2]\rho(r)$$

$$+[(3p+3p'-2)pp' - (p+p')\hat{L}^2]r\frac{d\rho(r)}{dr} + 2r^2 pp'\Delta\rho(r)\}dr .$$

$$(B13)$$

In the case $p=p'=L$ we recover from the above equations the results given in Eqs. (70), (73), and (74).

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