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Quantum-mechanical stress and a generalized virial theorem for clusters and solids

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Clusters and crystals are considered within the Born-Oppenheimer approximation. By means of the one-particle density matrix and the pair distribution a local stress tensor is defined with the divergence equal to the forces exerted upon the nuclei. From the local momentum balance follow (i) the stress theorem as a generalized virial theorem and (ii) an expression for the stress of a crystal involving integrals over the unit-cell surface. Within the Kohn-Sham formalism slightly modified expressions are obtained rigorously, and the form appropriate within the local-density approximation is given.

I. INTRODUCTION

Two tendencies may be observed in contemporary quantum chemistry and solid-state physics. On the one hand there has been much recent interest in considering the *global* properties of quantum-mechanical many-body systems like total energy and the quantities that can be derived therefrom.[1-4] On the other hand there is a tendency to emphasize and exploit the *local* point of view in the study of local properties and fragments of the system.[5] The theory of quantum mechanical stress and related quantities, whose basis was laid in the years around 1930,[6-13] comprises both of these aspects, and has been of increasing interest in the last few years. Recently the papers by Nielsen and Martin[14,15] and by Folland[16] have dealt with a variety of problems connected with this topic. These and other[4,5] papers also give references to earlier work. In addition surface stress has been treated by Needs and Godfrey[17] and Vanderbilt.[18]

The present paper[19] extends previous relations[20] for the hydrostatic pressure of a solid to the general case of stress, using reduced density matrices[21,22] throughout, within the many-body Schrödinger equation as well as the one-particle Kohn-Sham[23,24] description. We thereby complete the somewhat intuitive considerations given in Ref. 14 with respect to the transition from the many-body to the effectively one-particle description.

The key quantity is the stress $\overleftrightarrow{\sigma}$ of a finite neutral solid (a cluster) whose nuclei are considered as classical particles at fixed positions $\mathbf{R}_\ell$ with the electrons being in their ground state. As in Ref. 14, we define $\overleftrightarrow{\sigma}$ in terms of the derivative of the total energy E when a homogeneous, anisotropic and infinitesimal scaling is imposed upon the solid, i.e.

$$\overleftrightarrow{\sigma}\Omega_c = \sum_\ell \mathbf{R}_\ell \circ \frac{\partial}{\partial \mathbf{R}_\ell} E$$

with Ω_c being the volume of the cluster, the $\circ$ denoting a dyadic product of two vectors, and the sum running over the nuclear position parameters.

As regards the electronic many-body subsystem, the energy E is stationary with respect to first-order changes in the electronic wave function. This was used by Fock[25] to derive by an isotropic scaling the well known virial theorem of quantum mechanics, which in the case of Coulomb interactions reads $2T+V=3p\Omega_c$. Here T and V are the kinetic and potential energies, respectively, and p is the external pressure. Extending this procedure to anisotropic scalings one obtains a generalized virial theorem[14] which will be referred to as the "stress theorem". It relates the stress $\overleftrightarrow{\sigma}$ to electronic expectation values of appropriately defined tensor quantities, $\overleftrightarrow{\mathbf{T}}$ and $\overleftrightarrow{\mathbf{V}}$, i.e. $2\overleftrightarrow{\mathbf{T}}+\overleftrightarrow{\mathbf{V}}=-\overleftrightarrow{\sigma}\Omega_c$.

In the local approach to quantum mechanical stress the simplest local quantity is the electron density, whose associated electric field is well known to yield forces upon the nuclei through the Hellmann-Feynman theorem.[7-9] The density of these forces is related to the local stress tensor via the *local momentum balance*. Through a *local stress relation* (generalizing a local virial relation derived earlier[20]) we find an expression for the integral of the local stress over an arbitrary volume, which allows the following applications:

(i) For a finite cluster integration over all of space leads to a *global stress relation* for $2\overleftrightarrow{\mathbf{T}}+\overleftrightarrow{\mathbf{V}}$ and the generalized "virial" of the forces $\sum_\ell \mathbf{R}_\ell \circ \mathbf{F}_\ell$. With the help of the Hellmann-Feynman theorem this relation turns into the stress theorem for $\overleftrightarrow{\sigma}$. The interrelation between these three quantities is shown schematically in Fig. 1.

(ii) Choosing the integration volume as the unit cell of an infinite crystal the stress $\overleftrightarrow{\sigma}$ is expressed by the total momentum transfer through the unit cell surface. It consists of a "kinetic" quantum mechanical momentum transfer and the electrostatic interaction of the unit cell with its exterior.

These results for the stress are not immediately valid within the Kohn-Sham one-particle approach, despite its exactness. Therefore the above program is repeated using appropriate splittings of the one-particle density matrix and the electron pair distribution. Within the local-

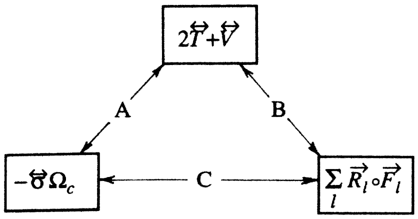

FIG. 1. Mutual relations between stress and related quantities: Eq. A ("stress theorem") follows from a scaling argument. Eq. B ("stress relation") follows from the local momentum balance. Eq. C follows from the Hellmann-Feynman theorem.

density approximation (LDA) the exchange-correlation (XC) contributions to the stress are explicitly evaluated, obtaining agreement with Ref. 14.

The paper is organized as follows: Sec. II deals with the many-body formulation. Section II A defines the Hamiltonian and distribution functions, and Sec. II B defines various ground-state expectation values. In Sec. II C we give relations for electrostatic force densities and the connection to the Hellmann-Feynman theorem. In Sec. II D is derived the local momentum balance for the local stress tensor, which in Sec. II E is used to derive local and global stress relations and the stress theorem. Section II F deals with the thermodynamic limit of an infinite system, and Sec. II G describes the separation of the stress into kinetic, Hartree and XC parts. This is required for the considerations in Sec. III, which briefly accomplishes the above procedure for the Kohn-Sham formalism. Finally in Sec. IV our results are summarized, and Appendixes A–D derive some of the relations required in the paper.

II. MANY-BODY THEORY OF STRESS IN CLUSTERS AND SOLIDS

We first consider an electrically neutral cluster of atoms (e.g., a large piece of an extended crystal) consisting of a finite number of nuclei and electrons, returning later to the thermodynamic limit of an infinite system. In this section the full many-body results for the ground-state of the electron system are given.

A. Hamiltonian and density matrices

Within the Born-Oppenheimer approximation of classically behaving nuclei the many-body Hamiltonian consists of the kinetic and potential terms, $\hat{H} = \hat{T} + \hat{V}$, with

$$\hat{T} = \sum_{i=1}^{N} \frac{\hat{\mathbf{p}}_i^2}{2m}, \tag{1}$$

where $\hat{\mathbf{p}}_i$ denotes the momentum operator and m the electron mass. N is the number of electrons, and the ^ denotes an operator quantity. The potential operator is separated according to the subsystem of nuclei (denoted by superscript "+") and electrons (denoted by superscript "−") as

$$\begin{aligned}\hat{V} &= V^{++} + \hat{V}^{+-} + \hat{V}^{--}\\ &= \frac{1}{2}\sum_{\ell\neq\ell'} \frac{Z_\ell Z_{\ell'}\epsilon^2}{|\mathbf{R}_\ell - \mathbf{R}_{\ell'}|} - \sum_{\ell,i} \frac{Z_\ell \epsilon^2}{|\mathbf{R}_\ell - \mathbf{r}_i|}\\ &\quad + \frac{1}{2}\sum_{i\neq j} \frac{\epsilon^2}{|\mathbf{r}_i - \mathbf{r}_j|},\end{aligned} \tag{2}$$

where ℓ and i label nuclei and electrons at positions $\mathbf{R}_\ell$ and $\mathbf{r}_i$, respectively. Z_ℓ denotes the nuclear charge and $\epsilon^2 = e^2/4\pi\varepsilon_0$ refers to the square of the elementary charge. In the following $\hbar$, m, $|e|$ and ϵ^2 are replaced by 1 using atomic Hartree units. The Hamiltonian given by Eqs. (1) and (2) thus describes a system with Coulomb interactions, but we do not consider more general interactions or magnetic fields in the present work.

We introduce charge densities and charge density operators for the particles, i.e., the nuclear charge density

$$\rho(\mathbf{r}) = \sum_\ell Z_\ell \delta(\mathbf{r} - \mathbf{R}_\ell) \tag{3a}$$

and the nuclear pair distribution

$$\rho(\mathbf{r}_1;\mathbf{r}_2) = \sum_{\ell\neq\ell'} Z_\ell Z_{\ell'} \delta(\mathbf{r}_1 - \mathbf{R}_\ell)\, \delta(\mathbf{r}_2 - \mathbf{R}_{\ell'}). \tag{3b}$$

The corresponding density operators for the electrons are

$$\hat{n}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \tag{4a}$$

and the pair distribution

$$\hat{n}(\mathbf{r}_1;\mathbf{r}_2) = \sum_{i\neq j} \delta(\mathbf{r}_1 - \mathbf{r}_i)\, \delta(\mathbf{r}_2 - \mathbf{r}_j). \tag{4b}$$

The self-interaction terms are eliminated in Eqs. (3b) and (4b).

The potential terms in Eq. (2) may be rewritten in terms of these density operators as

$$V^{++} = \frac{1}{2}\int d^3r_1 \int d^3r_2\, \rho(\mathbf{r}_1;\mathbf{r}_2)\frac{1}{r_{12}}, \tag{5a}$$

$$\hat{V}^{+-} = -\frac{1}{2}\int d^3r_1 \int d^3r_2\, [\rho(\mathbf{r}_1)\hat{n}(\mathbf{r}_2) + \hat{n}(\mathbf{r}_1)\rho(\mathbf{r}_2)]\frac{1}{r_{12}}, \tag{5b}$$

$$\hat{V}^{--} = \frac{1}{2}\int d^3r_1 \int d^3r_2 \hat{n}(\mathbf{r}_1;\mathbf{r}_2)\frac{1}{r_{12}} \tag{5c}$$

with $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ and $r_{12} = |\mathbf{r}_{12}|$. The potential operator $\hat{V}$ becomes

$$\hat{V} = \frac{1}{2}\int d^3r_1 \int d^3r_2 \hat{\nu}(\mathbf{r}_1;\mathbf{r}_2)\frac{1}{r_{12}} \tag{6}$$

with the total pair distribution operator $\hat{\nu}$ defined as

$$\begin{aligned}\hat{\nu}(\mathbf{r}_1;\mathbf{r}_2) &= \rho(\mathbf{r}_1;\mathbf{r}_2) - \rho(\mathbf{r}_1)\hat{n}(\mathbf{r}_2)\\ &\quad - \hat{n}(\mathbf{r}_1)\rho(\mathbf{r}_2) + \hat{n}(\mathbf{r}_1;\mathbf{r}_2).\end{aligned} \tag{7}$$

The analogous total density operator is

$$\hat{\nu}(\mathbf{r}) = \rho(\mathbf{r}) - \hat{n}(r). \tag{8}$$

Note that in defining the operators Eqs. (4)–(8) the general many-body operators are maintained. No expectation values are introduced up to this point.

B. Ground-state expectation values

The lowest-energy solution of the Schrödinger equation $\hat{H}\Phi = E\Phi$ defines the electron ground-state wave function $\Phi = \Phi(\mathbf{r}_1,\sigma_1;\ldots;\mathbf{r}_N,\sigma_N)$ and energy E, where $\mathbf{r}_i$ and σ_i are position and spin variables, respectively. The energy expectation value is

$$E = \langle \Phi | \hat{H} | \Phi \rangle \equiv \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V} \rangle \equiv T + V \,, \tag{9}$$

where we suppress the explicit reference to Φ for convenience.

The expectation values of the density operators are written as

$$n(\mathbf{r}) = \langle \hat{n}(\mathbf{r}) \rangle \tag{10a}$$

for the electron density and

$$n(\mathbf{r}_1;\mathbf{r}_2) = \langle \hat{n}(\mathbf{r}_1;\mathbf{r}_2) \rangle \tag{10b}$$

for the pair distribution function. These quantities are normalized as follows:

$$\int d^3r_2 \; n(\mathbf{r};\mathbf{r}_2) = (N-1)\, n(\mathbf{r}), \tag{10c}$$

$$\int d^3r \; n(\mathbf{r}) = N. \tag{10d}$$

The $n(\mathbf{r}_1;\mathbf{r}_2)$ is symmetric with respect to an exchange of $\mathbf{r}_1$ and $\mathbf{r}_2$.

The one-particle density matrix[21,22] is

$$n(\mathbf{r},\mathbf{r}') = \frac{1}{(N-1)!} \sum_{\sigma_1,\ldots,\sigma_N} \int d^3r_2 \cdots \int d^3r_N \Phi(\mathbf{r},\sigma_1;\mathbf{r}_2,\sigma_2;\ldots;\mathbf{r}_N,\sigma_N)\Phi^*(\mathbf{r}',\sigma_1;\mathbf{r}_2,\sigma_2;\ldots;\mathbf{r}_N,\sigma_N), \tag{11a}$$

whose diagonal is the electron density

$$n(\mathbf{r},\mathbf{r}) = n(\mathbf{r}) \,. \tag{11b}$$

Note that $n(\mathbf{r}_1;\mathbf{r}_2)$ with a ";" denotes the pair distribution, whereas $n(\mathbf{r},\mathbf{r}')$ with a "," denotes the one-particle density matrix.

The kinetic and potential energies may be written in terms of the one-particle density matrix and pair distribution functions as

$$T = \int d^3r \, \frac{\hat{\mathbf{p}}^2}{2} \, n(\mathbf{r},\mathbf{r}')\big|_{\mathbf{r}'=\mathbf{r}} \,, \tag{12}$$

$$V = \tfrac{1}{2} \int d^3r_1 \int d^3r_2 \nu(\mathbf{r}_1;\mathbf{r}_2) \frac{1}{r_{12}}. \tag{13}$$

Here the total pair distribution function $\nu(\mathbf{r}_1;\mathbf{r}_2)$ is the expectation value of Eq. (7).

C. Electrostatic force densities

We introduce the electrostatic potential $\phi(\mathbf{r})$ as the solution of the Poisson equation, i.e.

$$\phi(\mathbf{r}) = \int d^3r' \; \nu(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} = \phi^+(\mathbf{r}) + \phi^-(\mathbf{r}), \tag{14}$$

which by Eq. (8) is the sum of a nuclear potential $\phi^+(\mathbf{r})$ and an electronic Hartree potential $\phi^-(\mathbf{r})$.

The total electrostatic field is

$$\mathbf{E}(\mathbf{r}) = -\frac{\partial \phi(\mathbf{r})}{\partial \mathbf{r}} \equiv \mathbf{E}^+(\mathbf{r}) + \mathbf{E}^-(\mathbf{r}), \tag{15}$$

where

$$\mathbf{E}^+(\mathbf{r}) = \int d^3r_1 \; \rho(\mathbf{r}_1)\mathbf{E}_1(\mathbf{r}), \tag{16a}$$

$$\mathbf{E}^-(\mathbf{r}) = -\int d^3r_1 \; n(\mathbf{r}_1)\mathbf{E}_1(\mathbf{r}) \tag{16b}$$

with

$$\mathbf{E}_i(\mathbf{r}) = \frac{\mathbf{r}-\mathbf{r}_i}{|\mathbf{r}-\mathbf{r}_i|^3} \tag{17}$$

denoting the electric field arising from a unit point charge at $\mathbf{r}_i$.

The total electrostatic force density at a point $\mathbf{r}$ is

$$\mathbf{f}(\mathbf{r}) = \tfrac{1}{2} \int d^3r_1 \int d^3r_2 \; \nu(\mathbf{r}_1;\mathbf{r}_2)[\delta(\mathbf{r}-\mathbf{r}_1)\mathbf{E}_2(\mathbf{r}) + \delta(\mathbf{r}-\mathbf{r}_2)\mathbf{E}_1(\mathbf{r})], \tag{18}$$

which simply expresses the force on all particles at $\mathbf{r}$ in terms of electrostatic interactions among the particles. Because of the symmetry $\nu(\mathbf{r}_1;\mathbf{r}_2) = \nu(\mathbf{r}_2;\mathbf{r}_1)$ we can write the electrostatic force density Eq. (18) simply as

$$\mathbf{f}(\mathbf{r}) = \int d^3r_2 \; \nu(\mathbf{r};\mathbf{r}_2)\mathbf{E}_2(r). \tag{18'}$$

Using the definition of $\nu(\mathbf{r}_1;\mathbf{r}_2)$, Eq. (7), we may separate the force density as $\mathbf{f} = \mathbf{f}^+ + \mathbf{f}^-$ with the nuclear part

$$\mathbf{f}^+(\mathbf{r}) = \int d^3r_2 \; \rho(\mathbf{r};\mathbf{r}_2)\mathbf{E}_2(\mathbf{r}) + \rho(\mathbf{r})\mathbf{E}^-(\mathbf{r}) \tag{19a}$$

being the force density on the nuclear subsystem arising from all nuclei and electrons. The electron part $\mathbf{f}^-$ is

$$\mathbf{f}^-(\mathbf{r}) = -n(\mathbf{r})\mathbf{E}^+(\mathbf{r}) + \int d^3r_2 \; n(\mathbf{r};\mathbf{r}_2)\mathbf{E}_2(\mathbf{r}), \tag{19b}$$

i.e., the force density on the electrons at $\mathbf{r}$ due to the nuclei and electrons. We may call $\mathbf{f}^-$ the Ehrenfest force density since it is the force acting upon quantum mechanical particles in analogy with Ehrenfest's theorem[6] of the force upon a wave packet. Whereas $\mathbf{f}^-(\mathbf{r})$ is a smooth function of $\mathbf{r}$, the $\mathbf{f}^+(\mathbf{r})$ consists (due to the discreteness of the background) of δ-functions,

$$\mathbf{f}^+(\mathbf{r}) = \sum_{\ell} \mathbf{F}_{\ell}\delta(\mathbf{r}-\mathbf{R}_{\ell}) \tag{20}$$

with

$$\mathbf{F}_\ell = Z_\ell[\mathbf{E}(\mathbf{r})-Z_\ell\mathbf{E}_\ell(\mathbf{r})]_{\mathbf{r}=\mathbf{R}_\ell}\ , \tag{21}$$

i.e., the nuclear charge times the total electric field, Eqs. (16) less the nuclear self-interaction term. $\mathbf{E}_\ell(\mathbf{r})$ is given by Eq. (17), replacing $\mathbf{r}_i$ by $\mathbf{R}_\ell$.

The well-known Hellmann-Feynman theorem[7–9] states that for any eigenstate of the Hamiltonian, i.e., especially for the ground state, the force upon a classical nucleus at $\mathbf{R}_\ell$ is

$$-\frac{\partial\langle\hat{H}\rangle}{\partial\mathbf{R}_\ell} = -\left\langle\frac{\partial\hat{H}}{\partial\mathbf{R}_\ell}\right\rangle = -\left\langle\frac{\partial\hat{V}}{\partial\mathbf{R}_\ell}\right\rangle = \mathbf{F}_\ell \tag{22}$$

so that $\mathbf{f}^+(\mathbf{r})$ may be referred to as the "Hellmann-Feynman force density".

Since we consider only the electronic ground state of the system, there can be no net force or torque acting upon the subsystem of classically behaving nuclei, i.e.,

$$\int d^3r\ \mathbf{f}^+(\mathbf{r}) = 0, \tag{23a}$$

$$\int d^3r\ \mathbf{r}\times\mathbf{f}^+(\mathbf{r}) = 0. \tag{23b}$$

The latter relation may be reexpressed as a statement that the dyadic product $\mathbf{r}\circ\mathbf{f}^+(\mathbf{r})$ may have an antisymmetric part whose integral must vanish identically.

D. Local momentum balance

A local stress (or stress field) is defined, in analogy with the classical elasticity theory, as a tensor field whose divergence is equal to the force density. In a quantum system there are kinetic as well as potential stress fields, and following Ziesche and Lehmann[20] we introduce the (real) momentum flux density

$$2\overleftrightarrow{t}(\mathbf{r}) = \frac{\hat{\mathbf{p}}'^*+\hat{\mathbf{p}}}{2}\circ\frac{\hat{\mathbf{p}}'^*+\hat{\mathbf{p}}}{2}\ n(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}}\ . \tag{24}$$

In Appendix A it is shown that the divergence of $2\overleftrightarrow{t}(\mathbf{r})$ equals the electron force density, i.e.,

$$\frac{\partial}{\partial\mathbf{r}}\cdot 2\overleftrightarrow{t}(\mathbf{r}) = \mathbf{f}^-(\mathbf{r}). \tag{25}$$

This result was first given by Pauli[7] for a single electron, showing the microscopic balance of momentum flux and the force density. The quantity $-2\overleftrightarrow{t}(\mathbf{r})$ is referred to as the kinetic stress tensor field of the electrons.

The potential stress tensor field is defined as $-\overleftrightarrow{\eta}(\mathbf{r})$ with

$$\overleftrightarrow{\eta}(\mathbf{r}) = \tfrac{1}{2}\int d^3r_1\int d^3r_2\ v(\mathbf{r}_1;\mathbf{r}_2)\overleftrightarrow{\eta}_{12}(\mathbf{r}) \tag{26}$$

and

$$\overleftrightarrow{\eta}_{12}(\mathbf{r}) = -\frac{1}{4\pi}[\mathbf{E}_1(\mathbf{r})\circ\mathbf{E}_2(\mathbf{r}) + \mathbf{E}_2(\mathbf{r})\circ\mathbf{E}_1(\mathbf{r}) - \mathbf{E}_1(\mathbf{r})\cdot\mathbf{E}_2(\mathbf{r})\overleftrightarrow{1}], \tag{27}$$

where $\mathbf{E}_i(\mathbf{r})$ is the function (17). Note that $-\overleftrightarrow{\eta}_{12}(\mathbf{r})$ is the Maxwell stress tensor of two interacting unit point charges located at $\mathbf{r}_1$ and $\mathbf{r}_2$ less the self-interaction contribution of these charges:

$$\overleftrightarrow{\eta}_{12}(\mathbf{r}) = -\frac{1}{4\pi}\{[\mathbf{E}_1(\mathbf{r})+\mathbf{E}_2(\mathbf{r})]\circ[\mathbf{E}_1(\mathbf{r})+\mathbf{E}_2(\mathbf{r})]-\tfrac{1}{2}[\mathbf{E}_1(\mathbf{r})+\mathbf{E}_2(\mathbf{r})]^2\,\overleftrightarrow{1} - \mathbf{E}_1(\mathbf{r})\circ\mathbf{E}_1(\mathbf{r})+\tfrac{1}{2}\mathbf{E}_1(\mathbf{r})^2\,\overleftrightarrow{1}-\mathbf{E}_2(\mathbf{r})\circ\mathbf{E}_2(\mathbf{r})+\tfrac{1}{2}\mathbf{E}_2(\mathbf{r})^2\,\overleftrightarrow{1}\}\ . \tag{28}$$

(The prefactor ε_0 equals $1/4\pi$ in atomic units.) The divergence of $\overleftrightarrow{\eta}_{12}(\mathbf{r})$ is simple to calculate and we find the electrostatic momentum balance

$$\frac{\partial}{\partial\mathbf{r}}\cdot\overleftrightarrow{\eta}(\mathbf{r}) = -\mathbf{f}(\mathbf{r}), \tag{29}$$

see Appendix B.

A central result is the *local momentum balance,* which is found by adding Eqs. (25) and (29) to give

$$\frac{\partial}{\partial\mathbf{r}}\cdot\overleftrightarrow{\sigma}(\mathbf{r}) = \mathbf{f}^+(\mathbf{r}), \tag{30}$$

where we have defined

$$\overleftrightarrow{\sigma}(\mathbf{r}) = -[2\overleftrightarrow{t}(\mathbf{r})+\overleftrightarrow{\eta}(\mathbf{r})] \tag{31}$$

as the local stress tensor.

Note that it is only the nuclear force density $\mathbf{f}^+(\mathbf{r})$ that appears in Eq. (30). This is to be expected because Eq. (25) as a generalized Ehrenfest theorem contains only the force on the electrons, whereas Eq. (29) involves the total force density because it refers to all charges of the system. Thus the local stress tensor is related only to the forces on the nuclei which should be compensated by external forces keeping the nuclei in their given positions, according to the Born-Oppenheimer approximation.

Equation (30) specifies how to calculate atomic forces [i.e., $\mathbf{f}^+(\mathbf{r})$ defined by Eq. (20)] from the local stress tensor $\overleftrightarrow{\sigma}(\mathbf{r})$. The first derivation of the stress as the sum of a kinetic stress and a Maxwell stress, Eq. (31), was presented by Feynman,[13] and a form valid for general many-body interactions was given by Nielsen and Martin.[14] Regarding the stress fields as defined in Eqs. (24), (26)–(28), and (31), we remark that this is in no way a unique form, since the curl of an arbitrary tensor field may be added without affecting the physical force. This ambiguity or arbitrariness of the stress field is discussed also by Nielsen and Martin[14] and is related to the ambiguity of the electromagnetic energy density discussed by Feynman.[13,26]

As a final remark, the momentum balance (30) can be considered as a rigorous relation between the one-particle density matrix (or momentum distribution), the pair distribution function, and the electron density.

E. Local and global stress relations

Several interesting results follow from Eq. (30). Firstly, integration of Eq. (30) over an arbitrary volume Ω with a surface S gives

$$\int_\Omega d^3r\ \mathbf{f}^+(\mathbf{r}) = \int_S d\mathbf{S}\cdot\overleftrightarrow{\sigma}(\mathbf{r}), \tag{32}$$

which is the force exerted upon the fragment Ω of the cluster. The fragment could be chosen to include only a single nucleus, thus giving the force $\mathbf{F}_\ell$ on that nucleus in a way complementary to the Hellmann-Feynman theorem (21) and (22).

Secondly, there is a *local stress relation*

$$\overleftrightarrow{\sigma}(\mathbf{r}) = \frac{\partial}{\partial\mathbf{r}}\cdot\overleftrightarrow{\sigma}(\mathbf{r})\circ\mathbf{r} - \mathbf{f}^+(\mathbf{r})\circ\mathbf{r}, \tag{33}$$

which is found by multiplying Eq. (30) dyadically by $\mathbf{r}$ and using $\partial/\partial\mathbf{r}\circ\mathbf{r}=\overleftrightarrow{1}$. Integrating Eq. (33) over Ω gives

$$\int_\Omega d^3r\ \overleftrightarrow{\sigma}(\mathbf{r}) = \int_S d\mathbf{S}\cdot\overleftrightarrow{\sigma}(\mathbf{r})\circ\mathbf{r} - \int_\Omega d^3r\ \mathbf{f}^+(\mathbf{r})\circ\mathbf{r}, \tag{34}$$

which is the stress relation for the fragment Ω of the system.

If Ω is taken as all of space and the system is finite the surface integral vanishes because $\overleftrightarrow{\sigma}(\mathbf{r})$ as defined by Eq. (31) decays sufficiently rapidly. Then we have the *global stress relation*

$$2\overleftrightarrow{\mathbf{T}}+\overleftrightarrow{\mathbf{V}} = \sum_\ell \mathbf{R}_\ell\circ\mathbf{F}_\ell \tag{35}$$

with the tensor quantities defined as (kinetic and potential energy tensors, respectively)

$$\overleftrightarrow{\mathbf{T}} = \int d^3r\ \overleftrightarrow{\mathbf{t}}(\mathbf{r}) = \int d^3r\ \frac{\hat{\mathbf{p}}\circ\hat{\mathbf{p}}}{2}n(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}}\ , \tag{36a}$$

$$\overleftrightarrow{\mathbf{V}} = \int d^3r\ \overleftrightarrow{\eta}(\mathbf{r}) = \tfrac{1}{2}\int d^3r_1 \int d^3r_2 v(\mathbf{r}_1;\mathbf{r}_2)\frac{\mathbf{r}_{12}\circ\mathbf{r}_{12}}{r_{12}^3}, \tag{36b}$$

and the nuclear force $\mathbf{F}_\ell$ given by Eq. (21). On the right-hand side (r.h.s.) of Eq. (35) the symmetry property (23b) has been used. Eq. (36a) is obtained from Eq. (24) by partial integration, and in Eq. (36b) the result (B3) has been used. According to the Hellmann-Feynman theorem (22) the r.h.s. of Eq. (35) can be written as $-\sum_\ell \mathbf{R}_\ell\circ\partial E/\partial\mathbf{R}_\ell$.

The stress of a finite system (a cluster) occupying a volume Ω_c and being in equilibrium with external forces is defined in terms of the change of E due to a homogeneous, anisotropic and infinitesimal scaling as

$$\overleftrightarrow{\sigma} \equiv \frac{1}{\Omega_c}\sum_\ell \mathbf{R}_\ell\circ\frac{\partial}{\partial\mathbf{R}_\ell}E\ . \tag{37}$$

Comparison with Eqs. (34) and (35) shows that the stress defined from the total energy agrees with the *mean* local stress defined as $\int d^3r\overleftrightarrow{\sigma}(\mathbf{r})/\Omega_c$. Note that $\overleftrightarrow{\sigma}(\mathbf{r})$ is essentially nonzero only within Ω_c. From Eqs. (35) and (37) follows the *stress theorem*

$$2\overleftrightarrow{\mathbf{T}}+\overleftrightarrow{\mathbf{V}} = -\ \overleftrightarrow{\sigma}\Omega_c \tag{38}$$

derived by Nielsen and Martin[14] using a scaling argument [see their Eq. (7)]. An alternative derivation restricted to Coulomb interactions is given in Appendix C. Forming the trace of Eq. (38) yields the pressure p as

$$2T+V = 3p\Omega_c, \tag{39}$$

where we have used $\mathrm{tr}\overleftrightarrow{\mathbf{T}}=T$ and $\mathrm{tr}\overleftrightarrow{\mathbf{V}}=V$ with the expectation values (12) and (13). This result is also known as the *virial theorem*. It has been derived in a fashion similar to the present one in Ref. 20.

F. The thermodynamic limit

In the thermodynamic limit of an infinite crystal (i.e., $\Omega_c\rightarrow\infty$) all quantities have to be calculated per unit cell, i.e. integrals and expectation values refer to the unit cell volume $\Omega_0=\Omega_c/N_c$, where N_c is the number of unit cells. The limit must be taken in a special way to ensure that the surface integral in Eq. (34) remains zero and thus that the above results hold. The infinite crystal must be built by adding unit cells one by one, always maintaining a finite cluster which grows in such a way that Ω_c, $N_c\rightarrow\infty$ but with Ω_c/N_c remaining finite. The cluster must remain electrically neutral and have a vanishing macroscopic electric field. All extensive quantities have to be divided by N_c, the number of unit cells, before taking the thermodynamic limit, i.e.,

$$\frac{\overleftrightarrow{\mathbf{T}}}{N_c}\rightarrow\int_{\Omega_0} d^3r\ \overleftrightarrow{\mathbf{t}}(\mathbf{r})\ ,\quad \frac{\overleftrightarrow{\mathbf{V}}}{N_c}\rightarrow\int_{\Omega_0} d^3r\ \overleftrightarrow{\eta}(\mathbf{r})\ .$$

Equation (37) takes the form

$$\overleftrightarrow{\sigma} = \frac{1}{\Omega_0}\sum_{i=1}^{3}\mathbf{a}_i\circ\frac{\partial}{\partial\mathbf{a}_i}\varepsilon\ , \tag{37'}$$

where ε is the energy per unit cell and the $\mathbf{a}_i$ denote the lattice translation vectors.[27]

For the infinite system the stress $\overleftrightarrow{\sigma}$ times Ω_0 is equal to the left-hand side of Eq. (34) when the volume Ω is taken as the unit cell volume Ω_0. Let us furthermore assume that the nuclei occupy, for a given form of the unit cell, their equilibrium positions so that $\mathbf{F}_\ell=0$. The case of nonzero forces would require an averaging procedure, as described by Nielsen and Martin.[14,28] From Eq. (34) we have

$$\begin{aligned}\overleftrightarrow{\sigma}\Omega_0 &= \int_{\Omega_0} d^3r\ \overleftrightarrow{\sigma}(\mathbf{r}) = \int_{S_0} d\mathbf{S}\cdot\overleftrightarrow{\sigma}(\mathbf{r})\circ\mathbf{r}\\ &= \int_{S_0}[d\mathbf{S}\cdot\overleftrightarrow{\sigma}(\mathbf{r})\circ\mathbf{r}]_s,\end{aligned} \tag{40}$$

where S_0 is the unit cell surface. In the last step we have introduced the symmetrization $[a\circ b]_s=\frac{1}{2}(a\circ b+b\circ a)$ in order to enforce symmetry in the individual terms of $\overleftrightarrow{\sigma}$.

The kinetic part $-2\overleftrightarrow{\mathbf{t}}(\mathbf{r})$ of $\overleftrightarrow{\sigma}(\mathbf{r})$ is inserted into the surface integral, and the potential part $-\overleftrightarrow{\eta}(\mathbf{r})$ can be transformed as shown in Appendix D to give

$$\overleftrightarrow{\sigma}\Omega_0 = -\,\mathrm{Re}\int_{S_0}\left[[\mathbf{r}\circ\hat{\mathbf{p}}]_s\left[\frac{\hat{\mathbf{p}}'^{*}+\hat{\mathbf{p}}}{2}n(\mathbf{r},\mathbf{r}')d\mathbf{S}\right]\right]_{\mathbf{r}'=\mathbf{r}} - \int_{\Omega_0}d^3r_1\int_{\infty-\Omega_0}d^3r_2\,\nu(\mathbf{r}_1;\mathbf{r}_2)\tfrac{1}{2}\left[\mathbf{r}_1\circ\frac{\partial}{\partial\mathbf{r}_1}-\mathbf{r}_2\circ\frac{\partial}{\partial\mathbf{r}_2}\right]_s\frac{1}{r_{12}}. \tag{41}$$

The first term is connected with the momentum flux through the unit cell surface S_0. The second term is due to particles *inside* Ω_0 interacting with particles *outside* the unit cell Ω_0. Interactions between particles entirely inside or outside Ω_0 do *not* contribute to the stress $\overleftrightarrow{\sigma}$ given by Eq. (41). One may rewrite this term using Eq. (B4).

G. Exchange and correlation part of the electrostatic stress

The local stress tensor $\overleftrightarrow{\sigma}(\mathbf{r})$ given by Eq. (31) is the full many-body result for a system with Coulomb interactions. The kinetic stress $-2\overleftrightarrow{t}(\mathbf{r})$ is related to a one-particle quantity, whereas the potential stress $-\overleftrightarrow{\eta}(\mathbf{r})$ is related to the pair distribution and therefore contains explicitly what is referred to as exchange and correlation (XC) terms.

The electron pair distribution $n(\mathbf{r}_1;\mathbf{r}_2)$ may be split into a product Hartree term and a remainder XC term as

$$n(\mathbf{r}_1;\mathbf{r}_2) \equiv n(\mathbf{r}_1)n(\mathbf{r}_2) + n_{\mathrm{XC}}(\mathbf{r}_1;\mathbf{r}_2). \tag{42}$$

Taking into account Eq. (7), this allows the separation of $\overleftrightarrow{\eta}(\mathbf{r})$, Eq. (26), into Hartree and XC parts. The Hartree part is

$$\overleftrightarrow{\eta}_H(\mathbf{r}) = -\left[\overleftrightarrow{\eta}^M(\mathbf{r})-\sum_{\ell}\overleftrightarrow{\eta}^M_{\ell}(\mathbf{r})\right], \tag{43}$$

where $\overleftrightarrow{\eta}^M$ is the Maxwell stress due to the total electrostatic field (15), i.e.,

$$\overleftrightarrow{\eta}^M(\mathbf{r}) = \frac{1}{4\pi}[\mathbf{E}(\mathbf{r})\circ\mathbf{E}(\mathbf{r})-\tfrac{1}{2}\mathbf{E}(\mathbf{r})^2\,\overleftrightarrow{1}]. \tag{44}$$

From $\overleftrightarrow{\eta}^M$ are subtracted, as in Eq. (28), the nuclear self-interaction terms $\overleftrightarrow{\eta}^M_{\ell}$ given by Eq. (44) with $\mathbf{E}(\mathbf{r})$ replaced by the electrostatic field due to the ℓth nucleus, $\mathbf{E}_{\ell}(\mathbf{r})$ given by Eq. (17) substituting $\mathbf{r}_i$ by $\mathbf{R}_{\ell}$ and adding a factor Z_{ℓ}.

The XC part of $\overleftrightarrow{\eta}(\mathbf{r})$ is given by

$$\overleftrightarrow{\eta}_{\mathrm{XC}}(\mathbf{r}) = \tfrac{1}{2}\int d^3r_1\int d^3r_2\; n_{\mathrm{XC}}(\mathbf{r}_1;\mathbf{r}_2)\overleftrightarrow{\eta}_{12}(\mathbf{r}) \tag{45}$$

in analogy with Eq. (26).

The total stress tensor field can therefore be written as

$$\overleftrightarrow{\sigma}(\mathbf{r}) = -\,[2\overleftrightarrow{t}(\mathbf{r})+\overleftrightarrow{\eta}_H(\mathbf{r})+\overleftrightarrow{\eta}_{\mathrm{XC}}(\mathbf{r})]. \tag{46}$$

The $\overleftrightarrow{\eta}_H(\mathbf{r})$ is the simplest to calculate because it only requires knowledge of the electron density $n(\mathbf{r})$, in addition to the given density of nuclei $\rho(\mathbf{r})$. The kinetic term $\overleftrightarrow{t}(\mathbf{r})$ requires the one-particle density matrix $n(\mathbf{r},\mathbf{r}')$ which contains many-body effects. In principle $n(\mathbf{r},\mathbf{r}')$ is determined by the self-energy operator $\Sigma(\mathbf{r},\mathbf{r}';\varepsilon)$, which has recently been calculated approximately in the so-called GW approximation by Hybertsen and Louie,[29] Godby *et al.*,[30] and others.[31] Experimental determination of $n(\mathbf{r},\mathbf{r}')$ is discussed in Ref. 32. As regards the XC term $\overleftrightarrow{\eta}_{\mathrm{XC}}(\mathbf{r})$, little is known about the $n_{\mathrm{XC}}(\mathbf{r}_1;\mathbf{r}_2)$ and consequently we cannot comment at present upon the feasibility of actual calculations.

An additional remark concerns the contribution of the Hartree term $\overleftrightarrow{\eta}_H(\mathbf{r})$ to the stress $\overleftrightarrow{\sigma}$, which is contained in the last term of Eq. (41) through the Hartree term of $\nu(\mathbf{r}_1;\mathbf{r}_2)$, which is given by $\nu(\mathbf{r}_1)\nu(\mathbf{r}_2)$. For calculational reasons it may be appropriate to reextend the integration over $\mathbf{r}_2$ to all of space, which leaves Eq. (41) unchanged because the integrand is antisymmetric with respect to an interchange of $\mathbf{r}_1$ and $\mathbf{r}_2$. Since the integration volumes overlap in this case, one has to take care of the cancellation of the self-interaction divergences again. Accomplishing this, the $\overleftrightarrow{\eta}_H$ is given by

$$\begin{aligned}\int_{\Omega_0}d^3r\;\overleftrightarrow{\eta}_H(\mathbf{r}) = {}&-\sum_{\mathbf{R}_{\ell}\in\Omega_0}Z_{\ell}\left[\mathbf{r}\circ\frac{\partial}{\partial\mathbf{r}}\mathrm{tr}+\tfrac{1}{2}\overleftrightarrow{1}\right]\left[\overleftrightarrow{\phi}(\mathbf{r})-\frac{Z_{\ell}}{|\mathbf{r}-\mathbf{R}_{\ell}|}\;\frac{\mathbf{r}-\mathbf{R}_{\ell}}{|\mathbf{r}-\mathbf{R}_{\ell}|}\circ\frac{\mathbf{r}-\mathbf{R}_{\ell}}{|\mathbf{r}-\mathbf{R}_{\ell}|}\right]\Bigg|_{\mathbf{r}=\mathbf{R}_{\ell}}\\ &+\int_{\Omega_0}d^3r\;n(\mathbf{r})\left[\mathbf{r}\circ\frac{\partial}{\partial\mathbf{r}}\mathrm{tr}+\tfrac{1}{2}\,\overleftrightarrow{1}\right]\overleftrightarrow{\phi}(\mathbf{r})\end{aligned} \tag{41'}$$

with

$$\overleftrightarrow{\phi}(\mathbf{r}) = \int d^3r_2\;\nu(\mathbf{r}_2)\frac{\mathbf{r}_{12}\circ\mathbf{r}_{12}}{r_{12}^3}\Bigg|_{\mathbf{r}_1=\mathbf{r}}. \tag{41''}$$

This form is appropriate for the application of the Ewald technique because $\overleftrightarrow{\phi}(\mathbf{r})$ has the crystal periodicity.

III. DENSITY-FUNCTIONAL THEORY AND THE LDA

Within the density-functional theory[23] an effective one-particle equation was derived by Kohn and Sham[24] (denoted KS),

$$[\tfrac{1}{2}\hat{\mathbf{p}}^2+V(\mathbf{r})+V_{\mathrm{XC}}(\mathbf{r})]\phi_k(\mathbf{r}) = \varepsilon_k\phi_k(\mathbf{r}) \tag{47}$$

for the one-particle orbitals ϕ_k with eigenvalues ε_k. Whereas $V(\mathbf{r})=-\phi(\mathbf{r})$ arises from the electrostatic potential $\phi=\phi^{+}+\phi^{-}$ due to nuclei (ϕ^{+}) and electrons (ϕ^{-}, Hartree) as given by Eq. (14), the second term $V_{\mathrm{XC}}(\mathbf{r})$ is an effective XC potential. The total energy is

$$E = T_{\mathrm{KS}}+V_H+E_{\mathrm{XC}}[n(\mathbf{r})]\;, \tag{48}$$

where T_{KS} is the kinetic energy of the one-particle wave functions,

$$T_{\mathrm{KS}} = \sum_{k}^{\mathrm{occ}} \langle \phi_k | \tfrac{1}{2}\hat{\mathbf{p}}^2 | \phi_k \rangle \;, \tag{49a}$$

and V_H is the Hartree potential energy,

$$V_H = V^{++} - \int d^3r\; n(\mathbf{r})[\phi^{+}(\mathbf{r}) + \tfrac{1}{2}\phi^{-}(\mathbf{r})] \;. \tag{49b}$$

Here V^{++} is the nuclear electrostatic energy (5a). $E_{\mathrm{XC}}[n(\mathbf{r})]$ is a functional of the exact charge density which is

$$n(\mathbf{r}) = \sum_{k}^{\mathrm{occ}} |\phi_k(\mathbf{r})|^2 \;.$$

The XC potential is the functional derivative of E_{XC},

$$V_{\mathrm{XC}}(\mathbf{r}) = \frac{\delta E_{\mathrm{XC}}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \;. \tag{50}$$

A partitioning of the true density matrix $n(\mathbf{r},\mathbf{r}')$, Eq. (11a), is suggested by the form of T_{KS} as

$$\begin{aligned} n(\mathbf{r},\mathbf{r}') &\equiv \sum_{k}^{\mathrm{occ}} \phi_k(\mathbf{r})\phi_k(\mathbf{r}') + n_{\mathrm{XC}}(\mathbf{r},\mathbf{r}') \\ &= n_{\mathrm{KS}}(\mathbf{r},\mathbf{r}') + n_{\mathrm{XC}}(\mathbf{r},\mathbf{r}') \;. \end{aligned} \tag{51}$$

This allows writing the exact kinetic energy as $T = T_{\mathrm{KS}} + T_{\mathrm{XC}}$ where T and T_{XC} are given by Eq. (12) using the density matrices $n(\mathbf{r},\mathbf{r}')$ and $n_{\mathrm{XC}}(\mathbf{r},\mathbf{r}')$, respectively. Similarly the exact potential energy is written as $V = V_H + V_{\mathrm{XC}}$ through the partitioning (42) of the pair distribution function.

Since the KS equation (47) is derived variationally from the true total energy (48), there is a momentum balance condition for the KS kinetic stress tensor density $\overleftrightarrow{\mathbf{t}}_{\mathrm{KS}}(\mathbf{r})$ [given by inserting $n_{\mathrm{KS}}(\mathbf{r},\mathbf{r}')$ into Eq. (24)],

$$\frac{\partial}{\partial \mathbf{r}} \cdot 2\overleftrightarrow{\mathbf{t}}_{\mathrm{KS}}(\mathbf{r}) = -\, n(\mathbf{r})[\mathbf{E}(\mathbf{r}) + \mathbf{E}_{\mathrm{XC}}(\mathbf{r})] \tag{52}$$

following directly from Eq. (47) as shown in Appendix B. In addition to the electric field (15) the XC electric field $\mathbf{E}_{\mathrm{XC}}(\mathbf{r}) = \partial V_{\mathrm{XC}}/\partial \mathbf{r}$ appears. This result is analogous to the momentum balance (25) whose r.h.s. [given by Eq. (19b)] also consists of an uncorrelated Hartree term and an XC term, according to the splitting (42). Similarly there is an electrostatic momentum balance for the Hartree stress tensor (43)

$$\frac{\partial}{\partial \mathbf{r}} \cdot \overleftrightarrow{\eta}_H(\mathbf{r}) = -\, \mathbf{f}^{+}(\mathbf{r}) + n(\mathbf{r})\mathbf{E}(\mathbf{r}) \tag{53}$$

in analogy with Eqs. (29) and (19).

With these definitions the local stress tensor (31) is partitioned into KS and XC parts as $\overleftrightarrow{\sigma}(\mathbf{r}) \equiv \overleftrightarrow{\sigma}_{\mathrm{KS}}(\mathbf{r}) + \overleftrightarrow{\sigma}_{\mathrm{XC}}(\mathbf{r})$ with

$$\overleftrightarrow{\sigma}_{\mathrm{KS}}(\mathbf{r}) = -\, [2\overleftrightarrow{\mathbf{t}}_{\mathrm{KS}}(\mathbf{r}) + \overleftrightarrow{\eta}_H(\mathbf{r})] \;. \tag{54}$$

They fulfill the momentum balances

$$\frac{\partial}{\partial \mathbf{r}} \cdot \overleftrightarrow{\sigma}_{\mathrm{KS}}(\mathbf{r}) = \mathbf{f}^{+}(\mathbf{r}) + n(\mathbf{r})\mathbf{E}_{\mathrm{XC}}(\mathbf{r}) \;, \tag{55a}$$

$$\frac{\partial}{\partial \mathbf{r}} \cdot \overleftrightarrow{\sigma}_{\mathrm{XC}}(\mathbf{r}) = -\, n(\mathbf{r})\mathbf{E}_{\mathrm{XC}}(\mathbf{r}) \;. \tag{55b}$$

Equation (55a) follows from the sum of Eqs. (52) and (53), and Eq. (55b) is a consequence of Eqs. (30) and (55a). From the XC momentum balance (55b) follows in analogy to Eq. (33)

$$\overleftrightarrow{\sigma}_{\mathrm{XC}}(\mathbf{r}) = \frac{\partial}{\partial \mathbf{r}} \cdot \overleftrightarrow{\sigma}_{\mathrm{XC}}(\mathbf{r}) \circ \mathbf{r} + n(\mathbf{r})\mathbf{E}_{\mathrm{XC}}(\mathbf{r}) \circ \mathbf{r} \;, \tag{55c}$$

which can be considered a local and dyadic generalization of the Averill-Painter relation

$$2T_{\mathrm{XC}} + V_{\mathrm{XC}} = -\int d^3r\; n(\mathbf{r})\, \mathbf{r} \cdot \mathbf{E}_{\mathrm{XC}}(\mathbf{r}) \;, \tag{55d}$$

of Ref. 33.

We have thus shown that the local stress tensor $\overleftrightarrow{\sigma}(\mathbf{r})$ is given within the density-functional theory as the sum of a local KS stress $\overleftrightarrow{\sigma}_{\mathrm{KS}}(\mathbf{r})$ given by Eq. (54) and a local XC stress $\overleftrightarrow{\sigma}_{\mathrm{XC}}(\mathbf{r})$ determined by Eq. (55b) for a given form of the XC potential $V_{\mathrm{XC}}(\mathbf{r})$. Having solved Eq. (55b) it follows that all results in Sec. II have analogous expressions within density-functional theory.

For example, the force upon a fragment Ω of the system is given by Eq. (32) as

$$\int_{\Omega} d^3r\; \mathbf{f}^{+}(\mathbf{r}) = \int_{S} d\mathbf{S} \cdot [\overleftrightarrow{\sigma}_{\mathrm{KS}}(\mathbf{r}) + \overleftrightarrow{\sigma}_{\mathrm{XC}}(\mathbf{r})] \;. \tag{56}$$

The r.h.s. consists of a KS kinetic term and a Hartree potential term, and additionally a *local* XC term evaluated on the surface S. Similarly the stress theorem (38) has a term from the XC stress

$$\int d^3r\; [\overleftrightarrow{\sigma}_{\mathrm{KS}}(\mathbf{r}) + \overleftrightarrow{\sigma}_{\mathrm{XC}}(\mathbf{r})] = \overleftrightarrow{\sigma}\Omega_c \;. \tag{57}$$

Taking the thermodynamic limit we obtain the result

$$\begin{aligned} \overleftrightarrow{\sigma}\Omega_0 = &-\mathrm{Re} \int_{S_0} \left[[\mathbf{r} \circ \hat{\mathbf{p}}]_s \left[\frac{\hat{\mathbf{p}}'^{*} + \hat{\mathbf{p}}}{2} n_{\mathrm{KS}}(\mathbf{r},\mathbf{r}') d\mathbf{S} \right] \right]_{\mathbf{r}'=\mathbf{r}} \\ &- \int_{\Omega_0} d^3r_1 \int_{\infty-\Omega_0} d^3r_2\, \nu(r_1)\nu(r_2) \tfrac{1}{2} \left[\mathbf{r}_1 \circ \frac{\partial}{\partial \mathbf{r}_1} - \mathbf{r}_2 \circ \frac{\partial}{\partial \mathbf{r}_2} \right]_s \frac{1}{r_{12}} + \int_{S_0} [d\mathbf{S} \circ \mathbf{r}]_s\, \overleftrightarrow{\sigma}_{\mathrm{XC}}(\mathbf{r}) \end{aligned} \tag{58}$$

analogous to Eq. (41).

Up to this point our analysis rests upon rigorous relations. For practical calculations we now describe the corresponding results within the local-density approximation (LDA)[24] which assumes the form for the XC energy

$$E_{\mathrm{XC}}[n(\mathbf{r})] = \int d^3r\; n(\mathbf{r})\varepsilon_{\mathrm{XC}}^{\mathrm{h}}(n(\mathbf{r})) \;, \tag{59}$$

where $\varepsilon^{\mathrm{h}}_{\mathrm{XC}}(n)$ is the XC energy per particle in a homogeneous electron gas of density n. Thus the XC potential and the XC field are given by

$$V^{\mathrm{LDA}}_{\mathrm{XC}}(\mathbf{r}) = \left.\frac{d}{dn} n \varepsilon^{\mathrm{h}}_{\mathrm{XC}}\right|_{n=n(\mathbf{r})} , \tag{60}$$

$$n(\mathbf{r})\mathbf{E}^{\mathrm{LDA}}_{\mathrm{XC}}(\mathbf{r}) = \frac{\partial n(\mathbf{r})}{\partial \mathbf{r}} \left[n \frac{d^2}{dn^2} n \varepsilon^{\mathrm{h}}_{\mathrm{XC}} \right]_{n=n(\mathbf{r})} . \tag{61}$$

With the operator identity

$$n \frac{d^2}{dn^2} n = \frac{d}{dn} n^2 \frac{d}{dn}$$

Eq. (55b) takes the form

$$\frac{\partial}{\partial \mathbf{r}} \cdot \overleftrightarrow{\sigma}^{\mathrm{LDA}}_{\mathrm{XC}}(\mathbf{r}) = - \frac{\partial}{\partial \mathbf{r}} \left[n^2 \frac{d}{dn} \varepsilon^{\mathrm{h}}_{\mathrm{XC}}(n) \right]_{n=n(\mathbf{r})} , \tag{62}$$

from which we obtain the particular solution (see end of Sec. II D)

$$\overleftrightarrow{\sigma}^{\mathrm{LDA}}_{\mathrm{XC}}(\mathbf{r}) = - \left. n^2 \frac{d}{dn} \varepsilon^{\mathrm{h}}_{\mathrm{XC}}(n) \right|_{n=n(\mathbf{r})} \overleftrightarrow{1} \tag{63a}$$

being in agreement with the stress of a homogeneous electron gas, $\overleftrightarrow{\sigma}^{\mathrm{h}}(n) = -n^2[d\varepsilon^{\mathrm{h}}(n)/dn]\overleftrightarrow{1}$, and with the idea of the local nature of the LDA. As the final expression we rewrite Eq. (63a) as

$$\overleftrightarrow{\sigma}^{\mathrm{LDA}}_{\mathrm{XC}}(\mathbf{r}) = n(\mathbf{r})[\varepsilon^{\mathrm{h}}_{\mathrm{XC}}(n(\mathbf{r})) - V^{\mathrm{LDA}}_{\mathrm{XC}}(\mathbf{r})]\, \overleftrightarrow{1} . \tag{63b}$$

When this expression is inserted into Eq. (58), agreement is obtained with the results of Nielsen and Martin[14] [their Eq. (30)] for the LDA stress tensor, and we have thus provided a rigorous basis for their results.

IV. CONCLUSIONS

Formulas for the stress tensor $\overleftrightarrow{\sigma}$ of finite clusters as well as homogeneously strained infinite crystals are derived:

(i) From the many-body Schrödinger equation follows via its local momentum balance (30) the stress formula (41), which requires the knowledge of the one-particle density matrix $n(\mathbf{r},\mathbf{r}')$ and the electron pair distribution $n(\mathbf{r}_1;\mathbf{r}_2)$.

(ii) From the one-particle Kohn-Sham equation follows via its local momentum balances [Eqs. (55)] the stress formula (58), which requires for a given form of the XC-potential the self-consistent solutions of the Kohn-Sham equation and the solution of the equation for the local XC stress, Eq. (55b). In the local-density approximation this solution is given by Eq. (63b).

Corresponding pressure formulas arise simply by forming the trace of the mentioned stress formulas.

Consequences of these results are as follows:

(i) A force sum rule for the nonrelaxed surface of a semi-infinite crystal follows from the trace of Eq. (35) in the thermodynamic limit.[34,35]

(ii) The local momentum balances (25) or (30) can be viewed as relations between the one-particle density matrix $n(\mathbf{r},\mathbf{r}')$ and the pair distribution $n(\mathbf{r}_1;\mathbf{r}_2)$ in addition to the normalization conditions (10c) and Ref. 36.

(iii) The Kohn-Sham momentum balances (52) or (55a) relate the Kohn-Sham density matrix $n_{\mathrm{KS}}(\mathbf{r},\mathbf{r}')$ to the XC-potential of the Kohn-Sham equation.

(iv) The local stress relation (55c) for the XC parts of the momentum flux and the Maxwell stress tensor is a local and tensor generalization of the (global and scalar) Averill-Painter relation.[33]

(v) Finally is emphasized (as in Refs. 14 and 20) the possibility to calculate Hellmann-Feynman forces (which drive relaxations in clusters, around point defects, or at surfaces and interfaces) from surface integrals around individual nuclei [see Eq. (56)] or between parts of the cluster or crystal under consideration.

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APPENDIX A: LOCAL MOMENTUM BALANCES OF THE SCHRÖDINGER AND KOHN-SHAM EQUATIONS

The equation of motion for the one-particle density matrix is given by

$$\begin{aligned} 0 &= \frac{-i}{(N-1)!} \sum_{\sigma_1,\ldots,\sigma_N} \int d^3r_2 \cdots \int d^3r_N (H'-H)\Phi(\mathbf{r}_1,\sigma_1;\mathbf{r}_2,\sigma_2;\ldots;\mathbf{r}_N,\sigma_N) \\ &\qquad \times \Phi^*(\mathbf{r}'_1,\sigma_1;\mathbf{r}'_2,\sigma_2;\ldots;\mathbf{r}'_N,\sigma_N)\big|_{\mathbf{r}_1=\mathbf{r};\mathbf{r}'_1=\mathbf{r}';\mathbf{r}'_i=\mathbf{r}_i(i=2,\ldots,N)} \\ &= \left[\frac{\partial}{\partial \mathbf{r}'} + \frac{\partial}{\partial \mathbf{r}}\right] \mathbf{j}(\mathbf{r},\mathbf{r}') - i \int d^3r_2\, [-n(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}_2) + n(\mathbf{r},\mathbf{r}';\mathbf{r}_2)][\phi_2(\mathbf{r}') - \phi_2(\mathbf{r})] , \end{aligned} \tag{A1}$$

where the abbreviations $\phi_2(\mathbf{r}) = 1/|\mathbf{r}-\mathbf{r}_2|$ and

$$j(\mathbf{r},\mathbf{r}') = \frac{\underline{\hat{\mathbf{p}}'^* + \hat{\mathbf{p}}}}{2} n(\mathbf{r},\mathbf{r}') \tag{A2}$$

(the one-particle flux density matrix) are introduced. The quantity $n(\mathbf{r},\mathbf{r}';\mathbf{r}_2)$ is given by Eq. (11a) replacing the operator $\int d^3r_2$ by the factor $(N-1)$. In the first term of Eq. (A1) is used the identity

$$-i(\tfrac{1}{2}\hat{\mathbf{p}}'^2-\tfrac{1}{2}\hat{\mathbf{p}}^2)n(\mathbf{r},\mathbf{r}') = \left[\frac{\partial}{\partial\mathbf{r}'}+\frac{\partial}{\partial\mathbf{r}}\right]\frac{\hat{\mathbf{p}}'^*+\hat{\mathbf{p}}}{2}n(\mathbf{r},\mathbf{r}') = \left[\frac{\partial}{\partial\mathbf{r}'}+\frac{\partial}{\partial\mathbf{r}}\right]\mathbf{j}(\mathbf{r},\mathbf{r}') . \tag{A3}$$

For $\mathbf{r}'=\mathbf{r}$ from Eq. (A1) the continuity equation $\partial\mathbf{j}(\mathbf{r})/\partial\mathbf{r}=0$ arises. Application of $\hat{\mathbf{p}}$ before setting $\mathbf{r}'=\mathbf{r}$ immediately gives the momentum balance (26). This is seen from the definition (19b) of $\mathbf{f}^-(\mathbf{r})$ and from

$$\begin{aligned}\hat{\mathbf{p}}\circ\left[\frac{\partial}{\partial\mathbf{r}'}+\frac{\partial}{\partial\mathbf{r}}\right]\mathbf{j}(\mathbf{r},\mathbf{r}') &= \left[\frac{\hat{\mathbf{p}}'^*+\hat{\mathbf{p}}}{2}+\frac{\hat{\mathbf{p}}'+\hat{\mathbf{p}}}{2}\right]\circ\left[\frac{\partial}{\partial\mathbf{r}'}+\frac{\partial}{\partial\mathbf{r}}\right]\frac{\hat{\mathbf{p}}'^*+\hat{\mathbf{p}}}{2}n(\mathbf{r},\mathbf{r}')\Bigg|_{\mathbf{r}'=\mathbf{r}}\\ &= \left[\frac{\partial}{\partial\mathbf{r}'}+\frac{\partial}{\partial\mathbf{r}}\right]\frac{\hat{\mathbf{p}}'^*+\hat{\mathbf{p}}}{2}\circ\frac{\hat{\mathbf{p}}'^*+\hat{\mathbf{p}}}{2}n(\mathbf{r},\mathbf{r}')\Bigg|_{\mathbf{r}'=\mathbf{r}}+\tfrac{1}{2}\hat{\mathbf{p}}\circ\frac{\partial}{\partial\mathbf{r}}\mathbf{j}(\mathbf{r})\\ &= \frac{\partial}{\partial\mathbf{r}}2\overleftrightarrow{\mathbf{t}}(\mathbf{r}) ,\end{aligned} \tag{A4}$$

where the definition (24) of $\overleftrightarrow{\mathbf{t}}(\mathbf{r})$ and the continuity equation are used.

Starting with the KS equation (47) and using the definitions (51) of the KS density matrix $n_{\mathrm{KS}}(\mathbf{r},\mathbf{r}')$ and a rewriting similar to Eq. (A3), the equation of motion for the KS density matrix results:

$$\left[\frac{\partial}{\partial\mathbf{r}'}+\frac{\partial}{\partial\mathbf{r}}\right]\mathbf{j}_{\mathrm{KS}}(\mathbf{r},\mathbf{r}') - n_{\mathrm{KS}}(\mathbf{r},\mathbf{r}')[V_{\mathrm{KS}}(\mathbf{r}')-V_{\mathrm{KS}}(\mathbf{r})] = 0 , \tag{A5}$$

where $V_{\mathrm{KS}}(\mathbf{r})$ abbreviates $-\phi(\mathbf{r})+V_{\mathrm{XC}}(\mathbf{r})$. For $\mathbf{r}'=\mathbf{r}$ the continuity equation $\partial\mathbf{j}_{\mathrm{KS}}(\mathbf{r})/\partial\mathbf{r}=0$ arises, which implies that also $\mathbf{j}_{\mathrm{XC}}$ has to obey the continuity equation. Now $\hat{\mathbf{p}}$ is applied and afterwards $\mathbf{r}'$ is set equal to $\mathbf{r}$. With $\partial V_{\mathrm{KS}}(\mathbf{r})/\partial\mathbf{r}=\mathbf{E}(\mathbf{r})+\mathbf{E}_{\mathrm{XC}}(\mathbf{r})$ and with a rewriting similar to Eq. (A4) the KS momentum balance (52) results from Eq. (A5).

APPENDIX B: THE ELECTROSTATIC MOMENTUM BALANCE

From the definition of $\overleftrightarrow{\eta}_{12}(\mathbf{r})$, Eq. (27), it follows that

$$\frac{\partial}{\partial\mathbf{r}}\overleftrightarrow{\eta}_{12}(\mathbf{r}) = -\,[\delta(\mathbf{r}-\mathbf{r}_1)\mathbf{E}_2(\mathbf{r})+\delta(\mathbf{r}-\mathbf{r}_2)\mathbf{E}_1(\mathbf{r})] . \tag{B1}$$

Application of the operator $\frac{1}{2}\int d^3r_1\int d^3r_2\; v(\mathbf{r}_1;\mathbf{r}_2)$ immediately gives the electrostatic momentum balance (29) because of the definitions Eqs. (27) and (18′). On the other hand, with the identity $(\partial/\partial\mathbf{r})\circ\mathbf{r}=\overleftrightarrow{1}$ the integral

$$\int d^3r\;\overleftrightarrow{\eta}_{12}(\mathbf{r}) = \int d^3r\left[\frac{\partial}{\partial\mathbf{r}}\circ\mathbf{r}\right]\overleftrightarrow{\eta}_{12}(\mathbf{r}) \tag{B2}$$

can be rewritten by means of a partial integration and using Eq. (B1) as

$$\int d^3r\;\overleftrightarrow{\eta}_{12}(\mathbf{r}) = \mathbf{E}_2(\mathbf{r}_1)\circ\mathbf{r}_1+\mathbf{E}_1(\mathbf{r}_2)\circ\mathbf{r}_2 = \frac{\mathbf{r}_{12}\circ\mathbf{r}_{12}}{r_{12}^3} . \tag{B3}$$

In the last step the definition (17) of $\mathbf{E}_i(\mathbf{r})$ is used. An equivalent form of Eq. (B3) is

$$\left[\mathbf{r}_1\circ\frac{\partial}{\partial\mathbf{r}_1}+\mathbf{r}_2\circ\frac{\partial}{\partial\mathbf{r}_2}\right]\frac{1}{r_{12}} = -\frac{\mathbf{r}_{12}\circ\mathbf{r}_{12}}{r_{12}^3} . \tag{B4}$$

APPENDIX C: PROOF OF THE STRESS THEOREM

The stress theorem (38) can be derived by two alternative methods. Firstly, it may be proven by considering an infinitesimal homogeneous and anisotropic stretching of the wave function. This is a generalization of Fock's method[25] and has been accomplished in Ref. 14. Secondly, it may be proven by evaluating the commutator of the Hamiltonian with the generalized virial operator $\sum_i\mathbf{r}_i\circ\hat{\mathbf{p}}_i$. In the following the essential equivalence of these two approaches will be shown directly. The point is that the generalized virial operator is in a sense the generating operator for an infinitesimal scaling of the wave function as shown below. Having done this, we will prove (38) using the second approach.

To avoid derivatives with respect to tensor quantities we will describe the scaling of the wave function by $\mathbf{r}_i\rightarrow\mathbf{r}_i'=\mathbf{r}_i+\lambda\overleftrightarrow{\varepsilon}\mathbf{r}_i$ with λ being a scalar variable and $\overleftrightarrow{\varepsilon}$ an arbitrary constant and symmetric tensor. The correctly normalized wave function is (reference to the spin variables is omitted)

$$\Phi_\lambda(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \det(1+\lambda\overleftrightarrow{\varepsilon})^{N/2}\Phi(\mathbf{r}_1',\ldots,\mathbf{r}_N') .$$

With this wave function we form the expectation value of the unchanged Hamiltonian

$$\langle\Phi_\lambda\,|\,\hat{H}\,|\,\Phi_\lambda\rangle = \det(1+\lambda\overleftrightarrow{\varepsilon})^N\int d^3r_1\cdots\int d^3r_N\;\Phi^*(\mathbf{r}_1',\ldots,\mathbf{r}_N')\hat{H}\Phi(\mathbf{r}_1',\ldots,\mathbf{r}_N') \tag{C1}$$

and consider the derivative with respect to λ for $\lambda=0$ (note that $\Phi_{\lambda=0}$ is the unstretched wave function Φ). With the help of

$$\frac{\partial}{\partial\lambda}\det(1+\lambda\overleftrightarrow{\varepsilon})\Big|_{\lambda=0} = \mathrm{tr}\overleftrightarrow{\varepsilon}\,, \tag{C2}$$

$$\frac{\partial}{\partial\lambda}\Phi(\mathbf{r}_1{}',\ldots,\mathbf{r}_N{}')\Big|_{\lambda=0} = i\sum_i \mathbf{r}_i\,\overleftrightarrow{\varepsilon}\hat{\mathbf{p}}_i\Phi(\mathbf{r}_1,\ldots,\mathbf{r}_N) \tag{C3}$$

we obtain

$$\frac{\partial}{\partial\lambda}\langle\Phi_\lambda|\hat{H}|\Phi_\lambda\rangle\Big|_{\lambda=0} = N\mathrm{tr}\overleftrightarrow{\varepsilon}\langle\hat{H}\rangle + i\left\langle-\sum_i \hat{\mathbf{p}}_i\,\overleftrightarrow{\varepsilon}\mathbf{r}_i\hat{H}+\hat{H}\sum_i \mathbf{r}_i\,\overleftrightarrow{\varepsilon}\hat{\mathbf{p}}_i\right\rangle . \tag{C4}$$

Taking into account that $\hat{\mathbf{p}}_i\,\overleftrightarrow{\varepsilon}\mathbf{r}_i-\mathbf{r}_i\,\overleftrightarrow{\varepsilon}\hat{\mathbf{p}}_i=-i\,\mathrm{tr}\overleftrightarrow{\varepsilon}$, the last relation turns into

$$\frac{\partial}{\partial\lambda}\langle\Phi_\lambda|\hat{H}|\Phi_\lambda\rangle\Big|_{\lambda=0} = i\left\langle\left[\hat{H},\sum_i \mathbf{r}_i\,\overleftrightarrow{\varepsilon}\hat{\mathbf{p}}_i\right]\right\rangle . \tag{C5}$$

For Φ being an eigenstate of $\hat{H}$ the two sides of Eq. (C5) have to vanish. Setting the l.h.s. to zero gives the stress theorem[14], whereas setting the r.h.s. to zero gives

$$i\left\langle\left[\hat{H},\left[\sum_i \mathbf{r}_i\circ\hat{\mathbf{p}}_i\right]_s\right]\right\rangle=0\,, \tag{C6}$$

because $\overleftrightarrow{\varepsilon}$ is an arbitrary symmetric tensor. Together with the torque sum rule (23b) the last equation yields

$$i\left\langle\left[\hat{H},\sum_i \mathbf{r}_i\circ\hat{\mathbf{p}}_i\right]\right\rangle=0 \tag{C7}$$

showing the desired equivalence.

To derive the stress theorem from Eq. (C7) we consider first the commutator

$$i\left[\hat{H},\sum_i\mathbf{r}_i\circ\hat{\mathbf{p}}_i\right] = \sum_i\hat{\mathbf{p}}_i\circ\frac{\partial}{\partial\hat{\mathbf{p}}_i}\hat{T} - \sum_i \mathbf{r}_i\circ\frac{\partial}{\partial\mathbf{r}_i}\hat{V}\,. \tag{C8}$$

With

$$\sum_i\hat{\mathbf{p}}_i\circ\frac{\partial}{\partial\hat{\mathbf{p}}_i}\hat{T} = 2\hat{\overleftrightarrow{\mathbf{T}}} \tag{C9}$$

the generalized virial theorem reads

$$2\overleftrightarrow{\mathbf{T}} - \left\langle\sum_i \mathbf{r}_i\circ\frac{\partial}{\partial\mathbf{r}_i}\hat{V}\right\rangle = 0\,, \tag{C10}$$

the trace of which is the usual virial theorem. To specify Eq. (C10) for our problem we have to insert the concrete form of $\hat{V}$, Eq. (2). With

$$\left[\sum_i \mathbf{r}_i\circ\frac{\partial}{\partial\mathbf{r}_i} + \sum_\ell \mathbf{R}_\ell\circ\frac{\partial}{\partial\mathbf{R}_\ell}\right]\hat{V} = -\hat{\overleftrightarrow{\mathbf{V}}} \tag{C11}$$

[see Eqs. (36b) and (B4)] and using that $\hat{H}$ depends upon the nuclear positions only via the potential energy $\hat{V}$ we find

$$2\overleftrightarrow{\mathbf{T}} + \overleftrightarrow{\mathbf{V}} = -\sum_\ell \mathbf{R}_\ell\circ\left\langle\frac{\partial\hat{H}}{\partial\mathbf{R}_\ell}\right\rangle . \tag{C12}$$

Applying the Hellmann-Feynman theorem (22) on the r.h.s. gives finally the stress theorem (38).

APPENDIX D: PROOF OF EQUATION (41)

Using Eq. (29) for the potential stress tensor field $\overleftrightarrow{\eta}(\mathbf{r})$ one can write

$$\begin{aligned}\int_{S_0}[\mathbf{r}\circ\overleftrightarrow{\eta}(\mathbf{r})d\mathbf{S}]_s &= \int_{\Omega_0}d^3r\,\{\overleftrightarrow{\eta}(\mathbf{r})-[\mathbf{r}\circ\mathbf{f}(\mathbf{r})]_s\}\\ &= \int_{\Omega_0}d^3r\,\tfrac{1}{2}\int d^3r_1\int d^3r_2\;\nu(\mathbf{r}_1;\mathbf{r}_2)\overleftrightarrow{\mathbf{I}}_{12}(\mathbf{r})\end{aligned} \tag{D1}$$

with the definition

$$\begin{aligned}\overleftrightarrow{\mathbf{I}}_{12}(\mathbf{r}) \equiv \overleftrightarrow{\eta}_{12}(\mathbf{r}) - [\mathbf{r}\circ\{&\delta(\mathbf{r}-\mathbf{r}_1)\mathbf{E}_2(\mathbf{r})\\ &+\delta(\mathbf{r}-\mathbf{r}_2)\mathbf{E}_1(\mathbf{r})\}]_s\,,\end{aligned}$$

and $\overleftrightarrow{\eta}_{12}(\mathbf{r})$ defined by Eq. (27). The forces in the tensor $\overleftrightarrow{\mathbf{I}}_{12}(\mathbf{r})$ can be expressed by the potential $1/r_{12}$. Using Eq. (B4) it becomes

$$\begin{aligned}\overleftrightarrow{\mathbf{I}}_{12}(\mathbf{r}) = \overleftrightarrow{\mathbf{w}}_{12}(\mathbf{r}) &+ \tfrac{1}{2}[\delta(\mathbf{r}-\mathbf{r}_1)+\delta(\mathbf{r}-\mathbf{r}_2)]\\ &\times\left[\mathbf{r}_1\circ\frac{\partial}{\partial\mathbf{r}_1}+\mathbf{r}_2\circ\frac{\partial}{\partial\mathbf{r}_2}\right]\frac{1}{r_{12}}\,,\end{aligned} \tag{D2}$$

with

$$\overleftrightarrow{\mathbf{w}}_{12}(\mathbf{r}) = \overleftrightarrow{\eta}_{12}(\mathbf{r}) - \tfrac{1}{2}[\delta(\mathbf{r}-\mathbf{r}_1)+\delta(\mathbf{r}-\mathbf{r}_2)]\frac{\mathbf{r}_{12}\circ\mathbf{r}_{12}}{r_{12}^3}\,. \tag{D3}$$

The first term in Eq. (D2) does not contribute to Eq. (D1) for the following reasons. First, $\int d^3r\,\overleftrightarrow{\mathbf{w}}_{12}(\mathbf{r})=0$ is a consequence of Eq. (B3), and hence for a finite cluster the tensor field

$$\overleftrightarrow{\mathbf{w}}(\mathbf{r}) = \tfrac{1}{2}\int d^3r_1\int d^3r_2\;\nu(\mathbf{r}_1;\mathbf{r}_2)\overleftrightarrow{\mathbf{w}}_{12}(\mathbf{r}) \tag{D4}$$

has the same property, $\int d^3r\,\overleftrightarrow{\mathbf{w}}(\mathbf{r})=0$. On the other hand, in the thermodynamic limit of an extended periodic crystal $\overleftrightarrow{\mathbf{w}}(\mathbf{r})$ becomes a tensor field possessing the crystal periodicity. This is true because the total pair distribution $\nu(\mathbf{r}_1;\mathbf{r}_2)$ becomes a crystal periodic function and because this property is transferred to $\overleftrightarrow{\mathbf{w}}(\mathbf{r})$ through $\overleftrightarrow{\mathbf{w}}_{12}(\mathbf{r})$, which depends according to Eqs. (D3) and (27) upon $\mathbf{r}_1$ and $\mathbf{r}_2$ only via the differences $\mathbf{r}-\mathbf{r}_1$ and $\mathbf{r}-\mathbf{r}_2$. Therefore we may write, as in Sec. II F:

$$\frac{1}{N_c}\int d^3r\,\overleftrightarrow{\mathbf{w}}(\mathbf{r})\to\int_{\Omega_0}d^3r\,\overleftrightarrow{\mathbf{w}}(\mathbf{r})\,, \tag{D5}$$

and hence $\int_{\Omega_0}d^3r\,\overleftrightarrow{\mathbf{w}}(\mathbf{r})=0$. Finally, the last term of Eq. (D2) contributes to Eq. (D1) a term

$$\int_{\Omega_0} d^3r\, \tfrac{1}{2}\int d^3r_1 \int d^3r_2\; v(\mathbf{r}_1;\mathbf{r}_2)\overleftrightarrow{\mathbf{I}}_{12}(\mathbf{r}) = \int_{\Omega_0} d^3r_1 \int d^3r_2\; v(\mathbf{r}_1;\mathbf{r}_2)\tfrac{1}{2} \times \left[\mathbf{r}_1\circ\frac{\partial}{\partial\mathbf{r}_1} - \mathbf{r}_2\circ\frac{\partial}{\partial\mathbf{r}_2}\right]_s \frac{1}{r_{12}}\,, \tag{D6}$$

where $\int_{\Omega_0} d^3r\,\delta(\mathbf{r}-\mathbf{r}_i)=1$ for $\mathbf{r}_i\in\Omega_0$ and $=0$ otherwise has been used. The integrand is antisymmetric with respect to an interchange of $\mathbf{r}_1$ and $\mathbf{r}_2$. Therefore $\mathbf{r}_2\in\Omega_0$ does not contribute and only the integration over the region outside Ω_0 remains nonzero, i.e., we may restrict $\mathbf{r}_2$ as $\mathbf{r}_2\in(\infty-\Omega_0)$.

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notation. This quantity satisfies the perfect screening sum rule $\int d^3r_2\, h(\mathbf{r}_1;\mathbf{r}_2)n(\mathbf{r}_2) = -1$, and its average over the coupling constant determines the XC energy $E_{\mathrm{XC}}[n]$ of the density-functional theory (Ref. 23).

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