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Generalized-gradient-functional treatment of strain in density-functional perturbation theory

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The direct calculation of elastic and piezoelectric tensors utilizing density-functional perturbation theory has been extended to encompass generalized-gradient-approximation functionals. Expressions for the first- and second-order exchange-correlation potentials and energies are found to have structures particular to the strain perturbation.

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Density-functional perturbation theory[1] (DFPT) can be combined with the quantum-mechanical theory of stress[2] and the Berry-phase theory of polarization[3] to permit the direct calculation of such material properties as the elastic tensor, the piezoelectric tensor, and the internal strain coupling parameters. To this end, homogeneous strain must be introduced as a perturbation within the framework of DFPT, which involves certain subtleties and appears to require a treatment differing from that suitable for "ordinary" perturbations such as atomic displacements.[4,5] Several of the authors recently produced a metric tensor formulation of strain in DFPT, which places it on the same formal footing as other perturbations, and provides a framework for the systematic development of all the relevant terms entering into DFPT calculations.[6] These include first-order operators and potentials needed to find self-consistent first-order wave functions, and explicit second derivatives of the energy functional evaluated with ground-state "frozen" wave functions.[1] We shall refer to Ref. 6 as I, and refer to equations in that paper as Eq. (I-1), etc.

The analysis presented in I was restricted to local-density-approximation (LDA) functionals. The first-order exchange-correlation (xc) potential $V_{xc}^{(1)}(\mathbf{x})$ could be expressed as a simple product of a local xc kernel times the strain-induced first-order density. The frozen-wave-function contribution to the second-order xc energy was given as the integral of the product of the first-order potential times a first-order density, plus that of the ground-state potential $V_{xc}^{(0)}$ times second-strain derivatives of the density. This structure paralleled that previously found for atomic displacement perturbations.[1] The xc terms entering DFPT for gradient-corrected functionals such as the generalized gradient approximation[7–9] (GGA) have been shown to exhibit the same structure for atomic displacements,[10] although with the simple multiplicative kernel replaced by a more complex linear operator.[11] We will denote this structure as the "standard form."

The strain perturbation introduces a qualitatively different feature, since the strain perturbs the gradient operator itself, not merely the densities. This has been recognized in the analysis of stress for GGA functionals.[12] In this paper, we apply the methods of I to derive the DFPT strain response within the GGA. We find that the structure of the xc terms cannot be expressed in the standard form described above, but requires additional classes of terms and the introduction of two similar but distinct first-order potentials.

Following I, we shall concentrate on the plane-wave basis set and norm-conserving pseudopotentials.[13] It has been found that the exchange-correlation potentials entering into the Kohn-Sham equations[14] for GGA functionals have considerably more rapid spatial variation than corresponding LDA potentials, and require the use of significantly higher plane-wave cutoff energies to achieve comparable convergence. An effective solution to this problem was introduced by White and Bird.[15] Modern realizations of plane-wave density-functional theory perform local potential operations on wave functions on real-space grids, using fast Fourier transforms (FFT's) to cycle between real and reciprocal space representations.[16] The spatial integral defining the xc contribution to the density-functional energies is, in practice, approximated as a summation over the real-space FFT mesh. White and Bird observed that when this sum, rather than the integral it approximates, is taken as the fundamental definition of the xc energy and the density gradient is defined by the corresponding FFT, the potential consistently defined on the same spatial mesh leads to much more rapid convergence, comparable to that of the LDA.[15] We have developed the DFPT strain analysis for GGA strictly within the White and Bird functional form. Our results will be presented for the non-spin-polarized case, with a brief discussion of the straightforward extension to a spin-polarized treatment at the end.

The analysis of I expressed the entire density functional in reduced coordinates, designated by tildes. Conventional coordinates were related to these through primitive lattice vectors in Eqs. (I-20) and (I-21). Let us designate the FFT mesh within one unit cell by the set of N points $\{\mathbf{x}\}$ corresponding to the reduced-coordinate set $\{\tilde{\mathbf{x}}\}$, and the complementary subsets of reciprocal lattice vectors as $\{\mathbf{G}\}$ and $\{\tilde{\mathbf{G}}\}$.[17] The White and Bird xc energy functional is then

$$E_{xc}[n] = \frac{\Omega}{N}\sum_{\{\mathbf{x}'\}} f_{xc}(n(\mathbf{x}),\gamma(\mathbf{x})) = \frac{\Omega}{N}\sum_{\{\tilde{\mathbf{x}}'\}} f_{xc}(n(\tilde{\mathbf{x}}),\gamma(\tilde{\mathbf{x}})), \quad (1)$$

where Ω is the unit cell volume, n is the electron density, and $\gamma \equiv |\nabla n|^2$. While it is conventional to specify $|\nabla n|$ as the second argument of GGA functions, in fact only even powers

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of this quantity enter the widely used PW91 (Ref. 8) and PBE (Ref. 9) forms, and using the square simplifies our subsequent analysis. We also follow White and Bird in using the energy-density f_{xc} rather than the more common density-energy product $n\varepsilon_{xc}$.[15] The sums in Eq. (1) are term-by-term identical whether indexed by the real or reduced coordinate mesh.

The White and Bird form requires the gradient of n to be defined on the $\{\tilde{\mathbf{x}}\}$ mesh in a way consistent with the discrete Fourier representation of the charge density,

$$\tilde{\mathbf{g}}(\tilde{\mathbf{x}}) = \frac{1}{N} \sum_{\{\tilde{\mathbf{x}}'\},\{\tilde{\mathbf{G}}\}} i\tilde{\mathbf{G}} e^{2\pi i \tilde{\mathbf{G}}\cdot(\tilde{\mathbf{x}}-\tilde{\mathbf{x}}')} n(\tilde{\mathbf{x}}'), \tag{2}$$

where we have introduced $\tilde{\mathbf{g}}$ as our notation for ∇n expressed as a reduced reciprocal-space vector. The squared magnitude is then given in terms of the reciprocal-space metric tensor Υ_{ij} defined in Eq. (I-22) as

$$\gamma(\tilde{\mathbf{x}}) = \sum_{ij} \tilde{g}_i(\tilde{\mathbf{x}}) \Upsilon_{ij} \tilde{g}_j(\tilde{\mathbf{x}}), \tag{3}$$

where we follow the convention of I in denoting reduced coordinate component indices by $i,j,\ldots=1,2,3$. The White and Bird *xc* potential is given on the discrete $\{\tilde{\mathbf{x}}\}$ mesh as a set of ordinary partial derivatives rather than functional derivatives. The density is no longer treated as a function, but as a set of independent variables, one on each mesh point. This implies that $dn(\tilde{\mathbf{x}}')/dn(\tilde{\mathbf{x}}) = \delta_{\tilde{\mathbf{x}}'\tilde{\mathbf{x}}}$. Substituting Eqs. (2) and (3) into Eq. (1), and changing variables appropriately before carrying out the required derivatives, we find

$$\begin{aligned} V_{xc}^{(0)}(\tilde{\mathbf{x}}) \equiv \frac{N}{\Omega}\frac{\partial E_{xc}}{\partial n(\tilde{\mathbf{x}})} &= \frac{\partial f_{xc}(\tilde{\mathbf{x}})}{\partial n} \\ &+ \frac{2}{N} \sum_{\{\tilde{\mathbf{G}}\},\{\tilde{\mathbf{x}}'\}} i e^{2\pi i \tilde{\mathbf{G}}\cdot(\tilde{\mathbf{x}}'-\tilde{\mathbf{x}})} \frac{\partial f_{xc}(\tilde{\mathbf{x}}')}{\partial \gamma} \sum_{ij} \tilde{G}_i \Upsilon_{ij} \tilde{g}_j(\tilde{\mathbf{x}}'). \end{aligned} \tag{4}$$

A single term from the FFT summation in Eq. (2) has been selected by the Kronecker delta, and what was the "external" $\tilde{\mathbf{x}}$ sum from Eq. (1) now generates the spatial FFT in Eq. (4). Introducing $\tilde{\mathbf{x}}$ the argument of the f_{xc} derivatives is a shorthand notation indicating that they are to be evaluated with actual arguments $n(\tilde{\mathbf{x}})$, $\gamma(\tilde{\mathbf{x}})$. We have also taken advantage of the fact that Υ_{ij} is symmetric in its indices. Equation (4) is equivalent to Eq. (10) of Ref. 15.

We can now derive the strain derivatives of V_{xc} needed in the self-consistent Sternheimer equation of DFPT, Eq. (I-10). Following the conventions of I, all strains $\eta_{\alpha\beta}$ are Cartesian, with components labeled by $\alpha,\beta,\gamma,\ldots$. It is convenient to denote all contributions to the strain derivatives of the charge density by a single symbol incorporating both the explicit strain dependencies of the ground-state valence-electron density $n_e^{(0)}$ and the model core-charge density n_c, and the first-order charge $n^{(1)}$ arising from the wave-function perturbation, Eq. (I-8),

$$\begin{aligned} n^{(\alpha\beta)}(\tilde{\mathbf{x}}) &\equiv \partial n(\tilde{\mathbf{x}})/\partial \eta_{\alpha\beta} \\ &= -\delta_{\alpha\beta} n_e^{(0)}(\tilde{\mathbf{x}}) + \partial n_c(\tilde{\mathbf{x}})/\partial \eta_{\alpha\beta} + n^{(1,\alpha\beta)}(\tilde{\mathbf{x}}). \end{aligned} \tag{5}$$

The core-charge derivative is given by Eq. (I-64). The reduced gradient is dependent on strain only through the density, since the metric tensor does not occur in Eq. (2). The strain derivative of $\tilde{\mathbf{g}}$ is thus

$$\tilde{\mathbf{g}}^{(\alpha\beta)}(\tilde{\mathbf{x}}) \equiv \frac{\partial \tilde{\mathbf{g}}(\tilde{\mathbf{x}})}{\partial \eta_{\alpha\beta}} = \frac{1}{N} \sum_{\{\tilde{\mathbf{x}}''\},\{\tilde{\mathbf{G}}\}} i\tilde{\mathbf{G}} e^{2\pi i \tilde{\mathbf{G}}\cdot(\tilde{\mathbf{x}}-\tilde{\mathbf{x}}')} n^{(\alpha\beta)}(\tilde{\mathbf{x}}'). \tag{6}$$

The strain derivative of V_{xc}, denoted with a similar superscript, is straightforwardly found from Eq. (4),

$$\begin{aligned} V_{xc}^{(\alpha\beta)}(\tilde{\mathbf{x}}) = {} & \frac{\partial^2 f_{xc}(\tilde{\mathbf{x}})}{\partial n^2} n^{(\alpha\beta)}(\tilde{\mathbf{x}}) + \frac{\partial^2 f_{xc}(\tilde{\mathbf{x}})}{\partial n \partial \gamma} \sum_{ij} [\tilde{g}_i(\tilde{\mathbf{x}}) \Upsilon_{ij}^{(\alpha\beta)} \tilde{g}_j(\tilde{\mathbf{x}}) \\ & + 2\tilde{g}_i(\tilde{\mathbf{x}}) \Upsilon_{ij} \tilde{g}_j^{(\alpha\beta)}(\tilde{\mathbf{x}})] + \frac{2}{N} \sum_{\{\tilde{\mathbf{x}}'\},\{\tilde{\mathbf{G}}\}} i e^{2\pi i \tilde{\mathbf{G}}\cdot(\tilde{\mathbf{x}}'-\tilde{\mathbf{x}})} \\ & \times \Bigg\{ \frac{\partial^2 f_{xc}(\tilde{\mathbf{x}}')}{\partial n \partial \gamma} n^{(\alpha\beta)}(\tilde{\mathbf{x}}') \sum_{ij} \tilde{G}_i \Upsilon_{ij} \tilde{g}_j(\tilde{\mathbf{x}}') \\ & + \frac{\partial f_{xc}(\tilde{\mathbf{x}}')}{\partial \gamma} \sum_{ij} [\tilde{G}_i \Upsilon_{ij}^{(\alpha\beta)} \tilde{g}_j(\tilde{\mathbf{x}}') + \tilde{G}_i \Upsilon_{ij} \tilde{g}_j^{(\alpha\beta)}(\tilde{\mathbf{x}}')] \\ & + \frac{\partial^2 f_{xc}(\tilde{\mathbf{x}}')}{\partial \gamma^2} \sum_{ij} \tilde{G}_i \Upsilon_{ij} \tilde{g}_j(\tilde{\mathbf{x}}') \sum_{kl} [\tilde{g}_k(\tilde{\mathbf{x}}') \Upsilon_{kl}^{(\alpha\beta)} \tilde{g}_l(\tilde{\mathbf{x}}') \\ & + 2\tilde{g}_k(\tilde{\mathbf{x}}') \Upsilon_{kl} \tilde{g}_l^{(\alpha\beta)}(\tilde{\mathbf{x}}')] \Bigg\}, \end{aligned} \tag{7}$$

where $\Upsilon^{(\alpha\beta)}$ is the strain derivative of the metric tensor defined in Eq. (I-26). Equation (7) contains two classes of terms: the familiar linear-operator-on-first-order-charge terms of the standard form,[1,11] and new terms combining zero-order density gradients and metric-tensor derivatives. Only the first term remains in the LDA case, which reverts to the standard form and is equivalent to Eq. (I-60). In spite of its many terms, the computational effort involved in evaluating Eq. (7) is only slightly greater than that involved in obtaining $V_{xc}^{(0)}$ itself, as its FFT structure is the same as that of Eq. (4).

Next, we consider the frozen-wave-function contributions to the second-order energies. While in the following we will continue to use the same superscript notation for density and reduced-gradient strain derivatives, only the explicit derivatives represented by the first two terms of Eq. (5) are to be included, dropping the third "self-consistency" term. First, we will deal with the volume prefactor in Eq. (1), recalling Eq. (I-29),

$$\begin{aligned} \frac{\partial^2 E_{xc}}{\partial \eta_{\alpha\beta} \partial \eta_{\gamma\delta}} &= \delta_{\alpha\beta}\delta_{\gamma\delta} E_{xc}^{(0)} + \delta_{\alpha\beta} \frac{\Omega}{N} \frac{\partial (N E_{xc}/\Omega)}{\partial \eta_{\gamma\delta}} \\ &+ \delta_{\gamma\delta} \frac{\Omega}{N} \frac{\partial (N E_{xc}/\Omega)}{\partial \eta_{\alpha\beta}} + \frac{\Omega}{N} \frac{\partial^2 (N E_{xc}/\Omega)}{\partial \eta_{\alpha\beta} \partial \eta_{\gamma\delta}}. \end{aligned} \tag{8}$$

The first strain derivatives are

$$\frac{\partial(NE_{xc}/\Omega)}{\partial\eta_{\alpha\beta}} = \sum_{\{\tilde{\mathbf{x}}\}} \frac{\partial f_{xc}(\tilde{\mathbf{x}})}{\partial n} n^{(\alpha\beta)}(\tilde{\mathbf{x}}) + \sum_{\{\tilde{\mathbf{x}}\},ij} \frac{\partial f_{xc}(\tilde{\mathbf{x}})}{\partial\gamma}[\tilde{g}_i(\tilde{\mathbf{x}})\Upsilon_{ij}^{(\alpha\beta)}\tilde{g}_j(\tilde{\mathbf{x}}) + 2\tilde{g}_i(\tilde{\mathbf{x}})\Upsilon_{ij}\tilde{g}_j^{(\alpha\beta)}(\tilde{\mathbf{x}})]. \tag{9}$$

It is useful to rewrite Eq. (9). By substituting Eq. (6) for $g_j^{(\alpha\beta)}$ and interchanging summation indices, we can identify a subexpression equivalent to the right side of Eq. (4) and show

$$\frac{\partial(NE_{xc}/\Omega)}{\partial\eta_{\alpha\beta}} = \sum_{\{\tilde{\mathbf{x}}\}} V_{xc}^{(0)}(\tilde{\mathbf{x}}) n^{(\alpha\beta)}(\tilde{\mathbf{x}}) + \sum_{\{\tilde{\mathbf{x}}\},ij} \frac{\partial f_{xc}(\tilde{\mathbf{x}})}{\partial\gamma}\tilde{g}_i(\tilde{\mathbf{x}})\Upsilon_{ij}^{(\alpha\beta)}\tilde{g}_j(\tilde{\mathbf{x}}). \tag{10}$$

This form is to be preferred for evaluating the second derivatives, and is computationally efficient for the first-order terms.

Taking a second strain derivative of Eq. (10), we find

$$\begin{aligned}\frac{\partial^2(NE_{xc}/\Omega)}{\partial\eta_{\gamma\delta}\partial\eta_{\alpha\beta}} &= \sum_{\{\tilde{\mathbf{x}}\}} [V_{xc}^{(\gamma\delta)} n^{(\alpha\beta)} + V_{xc}^{(0)} n^{(\alpha\beta\gamma\delta)}] \\ &+ \sum_{\{\tilde{\mathbf{x}}\},ij} \frac{\partial^2 f_{xc}}{\partial n\partial\gamma}\tilde{g}_i\Upsilon_{ij}^{(\alpha\beta)}\tilde{g}_j n^{(\gamma\delta)} \\ &+ \sum_{\{\tilde{\mathbf{x}}\},ij} \frac{\partial f_{xc}}{\partial\gamma}[2\tilde{g}_i\Upsilon_{ij}^{(\alpha\beta)}\tilde{g}_j^{(\gamma\delta)} + \tilde{g}_i\Upsilon_{ij}^{(\alpha\beta\gamma\delta)}\tilde{g}_j] \\ &+ \sum_{\{\tilde{\mathbf{x}}\},ijkl} \frac{\partial^2 f_{xc}}{\partial\gamma^2}\tilde{g}_i\Upsilon_{ij}^{(\alpha\beta)}\tilde{g}_j[\tilde{g}_k\Upsilon_{kl}^{(\gamma\delta)}\tilde{g}_k \\ &+ 2\tilde{g}_k\Upsilon_{kl}\tilde{g}_l^{(\gamma\delta)}],\end{aligned} \tag{11}$$

where all spatial arguments are understood to be $\tilde{\mathbf{x}}$. The metric-tensor second derivative $\Upsilon^{(\alpha\beta\gamma\delta)}$ is given by Eq. (I-28). The density second derivative $n^{(\alpha\beta\gamma\delta)} = \delta_{\alpha\beta}\delta_{\gamma\delta}n_e + n_c^{(\alpha\beta\gamma\delta)}$, with the core contribution $n_c^{(\alpha\beta\gamma\delta)}$ given by Eq. (I-66), and $\tilde{g}_i^{(\alpha\beta\gamma\delta)}$ is given by Eq. (6) with $n^{(\alpha\beta)} \rightarrow n^{(\alpha\beta\gamma\delta)}$. Equation (11) does not have the standard form, nor does it appear to be symmetric under the interchange of the order of differentiation. However, substituting Eq. (7) for $V_{xc}^{(\alpha\beta)}$ in Eq. (11) and selectively regrouping terms, an explicitly symmetric expression can be recovered. Most terms in this expression can be reformulated as modified first-order potentials acting on first-order charge densities. This is both computationally efficient and easily combined with the remaining terms in Eq. (8) to give the following overall result,

$$\begin{aligned}\frac{\partial^2 E_{xc}}{\partial\eta_{\gamma\delta}\partial\eta_{\alpha\beta}} &= \frac{\Omega}{N}\sum_{\{\tilde{\mathbf{x}}\}}\left[\left(\delta_{\alpha\beta}V_{xc}^{(0)} + \frac{1}{2}V_{xc}^{*(\alpha\beta)}\right)n^{(\gamma\delta)}\right. \\ &\left. + \left(\delta_{\gamma\delta}V_{xc}^{(0)} + \frac{1}{2}V_{xc}^{*(\gamma\delta)}\right)n^{(\alpha\beta)} + V_{xc}^{(0)}n^{(\alpha\beta\gamma\delta)}\right] \\ &+ \frac{\Omega}{N}\sum_{\{\tilde{\mathbf{x}}\},ij}\frac{\partial f_{xc}}{\partial\gamma}\tilde{g}_i(\delta_{\alpha\beta}\Upsilon^{(\gamma\delta)} + \delta_{\gamma\delta}\Upsilon^{(\alpha\beta)} + \Upsilon_{ij}^{(\alpha\beta\gamma\delta)})\tilde{g}_j \\ &+ \frac{\Omega}{N}\sum_{\{\tilde{\mathbf{x}}\},ijkl}\frac{\partial^2 f_{xc}}{\partial\gamma^2}\tilde{g}_i\Upsilon_{ij}^{(\alpha\beta)}\tilde{g}_j\tilde{g}_k\Upsilon_{kl}^{(\gamma\delta)}\tilde{g}_l,\end{aligned} \tag{12}$$

where $V_{xc}^{*(\alpha\beta)}$ is defined by making the substitution $\Upsilon_{ij}^{(\alpha\beta)} \rightarrow 2\Upsilon_{ij}^{(\alpha\beta)}$ in Eq. (7).[18] The first sum in Eq. (12) is as close to the standard form as possible. However the appearance of the modified potential $V_{xc}^{*(\alpha\beta)}$ in the first term, rather than $V_{xc}^{(\alpha\beta)}$ itself as in the standard form is unexpected. We also find, as in the case of the first-order potential, additional terms that arise solely from the action of strain on the gradient operator itself. These are most efficiently evaluated just as written. While the notation in Eq. (12) is somewhat different from the LDA expression, Eq. (I-67), substituting the first two terms of Eq. (5) for $n^{(\alpha\beta)}$ and $n^{(\gamma\delta)}$ and dropping all gradient terms does reproduce that result.

As discussed in I, mixed second derivatives with respect to one strain and one atomic displacement are required to compute the atomic-relaxation contributions to the elastic and piezoelectric tensors. Following the notation of I, we first compute the reduced-atomic-displacement derivative of E_{xc},

$$\frac{\partial(NE_{xc}/\Omega)}{\partial\tilde{\tau}_{\kappa i}} = \sum_{\{\tilde{\mathbf{x}}\}} V_{xc}^{(0)}(\tilde{\mathbf{x}})\frac{n_c(\tilde{\mathbf{x}})}{\partial\tilde{\tau}_{\kappa i}}. \tag{13}$$

The strain derivative of this expression is now straightforwardly evaluated. Restoring the Ω/N factor, we find

$$\frac{\partial^2 E_{xc}}{\partial\eta_{\alpha\beta}\partial\tilde{\tau}_{\kappa i}} = \frac{\Omega}{N}\sum_{\{\tilde{\mathbf{x}}\}}\left[V_{xc}^{(\alpha\beta)}\frac{\partial n_c}{\partial\tilde{\tau}_{\kappa i}} + V_{xc}^{(0)}\left(\delta_{\alpha\beta}\frac{\partial n_c}{\partial\tilde{\tau}_{\kappa i}} + \frac{\partial^2 n_c}{\partial\eta_{\alpha\beta}\partial\tilde{\tau}_{\kappa i}}\right)\right]. \tag{14}$$

Expressions for the core-charge derivatives required here are described in I as simple modifications of Eqs. (I-64) and (I-66). The first-order potential in Eq. (14) is the actual $V_{xc}^{(\alpha\beta)}$ strain derivative given by Eq. (7), not the modified version required in Eq. (12). Once the nonstandard contributions to $V_{xc}^{(\alpha\beta)}$ have been taken into account, this second derivative is consistent with the standard form. Both the modified potential and the additional terms in Eq. (12) arise from the interplay of two strain derivatives acting on the gradient operator, whereas the atomic displacement perturbation affects only the density itself.

To avoid further complicating the above expressions, only the non-spin-polarized case was explicitly treated. The generalization of Eqs. (7), (12), and (14), to spin-polarized expressions is straightforward.[11] In the PW91 (Ref. 8) and PBE (Ref. 9) formulations of the GGA, the exchange portion of f_{xc} is strictly a sum of spin-up and spin-down terms. The correlation portion depends on both spin densities, but only on the gradient of the total density. Thus only one mixed-spin derivative, $\partial^2 f_{xc}/\partial n_\uparrow \partial n_\downarrow$, needs to be introduced.

The present results have been incorporated in the open-source ABINIT software package,[19] which utilizes the White and Bird form of the GGA.[15] They have been extensively tested by comparing DFPT calculations of elastic, piezoelectric, and internal strain force-response tensors with numerical derivatives of ground-state stresses, electrical polarizations, and atomic forces following the procedures discussed in I. Capabilities for treating reduced-atomic-displacement perturbations within a number of popular LDA and GGA formulations had already been incorporated in ABINIT,[19] so relaxed-atom elastic and piezoelectric tensors can now be readily obtained for all these functionals by appropriately combining a set of DFPT results.[20]

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[17] The mesh should be chosen so that for each $\mathbf{G}$ in the set, $-\mathbf{G}$ is also a member of the set in order for certain steps in the analysis to be strictly valid.

[18] This replacement applies only to the explicit $\Upsilon^{(\alpha\beta)}$ terms appearing in Eq. (7), not those contained in the core-charge derivatives $n_c^{(\alpha\beta)}$ through Eq. (I-64).

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