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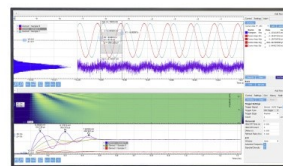
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# Generalized variational density functional perturbation theory

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We present an implementation of variational perturbation theory in the framework of density functional theory. We use an *ab initio* pseudopotential scheme with a plane wave basis set and expand the energy functional up to second order in the perturbation. The approach is fairly general and does not rely on the representativeness of the perturbation through a Hamiltonian operator and does not require the use of canonical orbitals. Instead, a functional formulation is used to characterize the perturbation. Several types of applications are presented which illustrate the variety of linear response phenomena that can be treated with our method (vibrational modes, Raman scattering, and nuclear magnetic resonance chemical shift computations). In combination with advanced gradient correction formulas, an accurate description of second order effects in periodic and isolated systems can be achieved. © 2000 American Institute of Physics.

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## I. INTRODUCTION

The outcome of many experiments measures the way in which a physical system reacts to the application of a small applied external field. If the external field is time independent, one can relate the measured response to the second order derivative of the total energy relative to appropriate fields. This is the case, for instance, for the electric polarizability or of the bulk modulus, which can be expressed as the second derivative of the energy relative to the external electric field and the volume, respectively. Given the relevance of this class of properties, a large number of methods has been devised to calculate static linear responses, and it has been implemented in the context of many approximated electron structure theories like Hartree–Fock, density functional theory,<sup>1</sup> Møller–Plesset perturbation theory,<sup>2</sup> or coupled clusters.<sup>3</sup> Here we shall focus on methods that can be applied within the density functional theory (DFT)<sup>4</sup> and, although our approach is fairly general, we shall present applications based on the plane wave (PW) pseudopotential scheme.

The simplest way to evaluate the response functions is to calculate the energy for various values of the applied field and extract numerically the energy derivatives. This procedure can work reasonably well, but it requires several evaluations of the total energy and the numerical derivative introduces errors. A more satisfactory approach is to evaluate directly the response functions, making use of perturbation theory. This leads, for the static response functions, to the familiar expression of the response function in terms of a double sum over the occupied and empty electronic states. This approach has been reformulated in the context of DFT by Baroni *et al.*<sup>5</sup> and successfully applied to many problems. An essential ingredient for the success of this approach has been the use of the Sternheimer method<sup>6</sup> which avoids explicit evaluation of the poorly convergent double sum and together with a good preconditioner leads to an efficient algorithm.

More recently Gonze and Gonze and Vigneron<sup>7</sup> have

shown that if one perturbs the Hamiltonian with an external field, the induced variation in the Kohn–Sham orbitals can be obtained to all perturbative orders from a variational formulation. Use of the  $2n+1$  theorem<sup>8</sup> then allows one to calculate the change in energy and the corresponding energy derivatives. For instance, the second order energy derivatives can be calculated once the first order variation in the Kohn–Sham orbitals is known. One advantage this theory has in common with the Sternheimer approach is that it avoids the need to perform explicitly the double summation. The efficiency of the variational density functional perturbation approach is comparable to that of Baroni *et al.*'s.<sup>5</sup>

The Gonze approach as well as the more standard perturbation theory are based on a Hamiltonian formulation. The purpose of this work is to generalize the Gonze variational approach to the case in which the perturbation cannot be expressed in Hamiltonian form. The need to treat such a term arises when, for instance, one wants to evaluate the effect of an electric field that couples with the polarization in a periodic system. Modern theories express the polarization in terms of a Berry phase,<sup>9</sup> which is not expressible in Hamiltonian terms. Furthermore, while conventional perturbation theory must be formulated in terms of Kohn–Sham eigenstates, there are times we need to work with other orbitals. A case in point is the calculation of nuclear magnetic resonance (NMR) chemical shifts which can profit from the use of maximally localized orbitals.<sup>10,11</sup>

Our derivation is very close to the spirit of DFT and in our opinion slightly more transparent than that of Gonze.<sup>7</sup> Of course our formulas reduce to those of Gonze in the case of Hamiltonian perturbations.

We will also address some technical problems, like the handling of gradient corrections or the choice of appropriate preconditioners. We will illustrate the performance of our method for the calculation of the vibrational frequencies, polarizability, Raman intensities and NMR chemical shifts.

## II. THEORY

In standard perturbation theory,<sup>7</sup> a small perturbation operator  $\lambda h$  is added to the Hamiltonian  $H$  of a system and its

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action evaluated. We propose a conceptually different approach using the variational principle in the framework of DFT.

Let us consider the Kohn–Sham (KS) density functional  $\mathcal{E}_{\text{KS}}[\{\varphi_i\}]$ . We work with the formulation of the Kohn–Sham functional in terms of nonorthogonal orbitals.<sup>12</sup> This can be realized by writing  $\mathcal{E}_{\text{KS}}$  in term of the density matrix  $\rho(\mathbf{r}, \mathbf{r}')$ :<sup>12,13</sup>

$$\begin{aligned} \mathcal{E}_{\text{KS}}[\rho(\mathbf{r}, \mathbf{r}')] = & -\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \delta(\mathbf{r} - \mathbf{r}') \nabla_{\mathbf{r}}^2 \rho(\mathbf{r}, \mathbf{r}') \\ & + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{|\rho(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} + \mathcal{E}_{\text{xc}}[\rho] \\ & + \mathcal{E}_{\text{ext}}[\rho], \end{aligned} \quad (1)$$

and expressing

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{ij} = \varphi_i^*(\mathbf{r}) S_{ij}^{-1} \varphi_j(\mathbf{r}'), \quad (2)$$

where  $S_{ij}^{-1}$  is the inverse of the overlap matrix  $S_{ij} = \langle \varphi_i | \varphi_j \rangle$ . The minimum of this functional is  $\mathcal{E}_{\text{KS}}^{(0)} \times [\{\varphi_i^{(0)}\}] = E^{(0)}$ , where we assume that (at the minimum) the orbitals are orthogonal,  $\langle \varphi_i^{(0)} | \varphi_j^{(0)} \rangle = \delta_{ij}$ .

Starting from  $\mathcal{E}_{\text{KS}}[\{\varphi_i\}]$  we add a perturbation functional of arbitrary form  $\mathcal{E}_{\text{KS}}^{\text{pert}}[\{\varphi_i\}]$  multiplied by  $\lambda$ , a small

perturbative parameter. This is meant to represent the interaction with a static, but otherwise arbitrarily, complex external field.

The total functional  $\mathcal{E}_{\text{KS}}^{\text{tot}}[\{\varphi_i\}] = \mathcal{E}_{\text{KS}}^{(0)}[\{\varphi_i\}] + \lambda \mathcal{E}_{\text{KS}}^{\text{pert}}[\{\varphi_i\}]$  will have a minimum which we shall expand perturbatively,

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots, \quad (3)$$

Similarly the KS orbitals that minimize  $\mathcal{E}_{\text{KS}}^{\text{tot}}$  can be expanded in  $\lambda$ :

$$\varphi_i = \varphi_i^{(0)} + \lambda \varphi_i^{(1)} + \lambda^2 \varphi_i^{(2)} + \dots \quad (4)$$

To the first order the charge density reads

$$n(\mathbf{r}) = n^{(0)}(\mathbf{r}) + \lambda n^{(1)}(\mathbf{r}) + \dots, \quad (5)$$

where

$$n^{(1)}(\mathbf{r}) = \sum_{i=1}^N [\varphi_i^{(0)*}(\mathbf{r}) \varphi_i^{(1)}(\mathbf{r}) + \varphi_i^{(1)*}(\mathbf{r}) \varphi_i^{(0)}(\mathbf{r})]. \quad (6)$$

In order to find perturbatively the minimum of  $\mathcal{E}_{\text{KS}}^{\text{tot}}$ ,

$$\begin{aligned} \mathcal{E}_{\text{KS}}^{\text{tot}} = & \mathcal{E}_{\text{KS}}^{(0)}[\{\varphi_i^{(0)}\}] + \lambda [\mathcal{E}_{\text{KS}}^{(0)}[\{\varphi_i^{(1)}\}] + \dots] \\ & + \lambda \mathcal{E}_{\text{KS}}^{\text{pert}}[\{\varphi_i^{(0)}\}] + \lambda [\mathcal{E}_{\text{KS}}^{\text{pert}}[\{\varphi_i^{(1)}\}] + \dots], \end{aligned} \quad (7)$$

we functionally expand  $\mathcal{E}_{\text{KS}}^{\text{tot}}$  to quadratic order:

$$\begin{aligned} \mathcal{E}_{\text{KS}}^{\text{tot}} = & \mathcal{E}_{\text{KS}}^{(0)}[\{\varphi_i^{(0)}\}] + \lambda \mathcal{E}_{\text{KS}}^{\text{pert}}[\{\varphi_i^{(0)}\}] + \frac{1}{2} \lambda^2 \sum_{i,j=1,N} \left\{ \langle \varphi_i^{(1)} | \langle \varphi_j^{(1)} | \frac{\delta^2 \mathcal{E}_{\text{KS}}^{(0)}}{\delta \langle \varphi_i^{(0)} | \delta \langle \varphi_j^{(0)} |} + \langle \varphi_j^{(1)} | \frac{\delta^2 \mathcal{E}_{\text{KS}}^{(0)}}{\delta \langle \varphi_j^{(0)} | \delta | \varphi_i^{(0)} \rangle} | \varphi_i^{(1)} \rangle \right. \\ & \left. + \langle \varphi_i^{(1)} | \frac{\delta^2 \mathcal{E}_{\text{KS}}^{(0)}}{\delta | \varphi_j^{(0)} \rangle \delta \langle \varphi_i^{(0)} |} | \varphi_j^{(1)} \rangle + \frac{\delta^2 \mathcal{E}_{\text{KS}}^{(0)}}{\delta | \varphi_i^{(0)} \rangle \delta | \varphi_j^{(0)} \rangle} | \varphi_i^{(1)} \rangle | \varphi_j^{(1)} \rangle \right\} + \lambda^2 \sum_{i=1}^N \left\{ \langle \varphi_i^{(1)} | \frac{\delta \mathcal{E}_{\text{KS}}^{\text{pert}}}{\delta \langle \varphi_i^{(0)} |} + \frac{\delta \mathcal{E}_{\text{KS}}^{\text{pert}}}{\delta | \varphi_i^{(0)} \rangle} | \varphi_i^{(1)} \rangle \right\} + O(\lambda^3), \end{aligned} \quad (8)$$

where we have used the fact that

$$\frac{\delta \mathcal{E}_{\text{KS}}^{(0)}}{\delta \langle \varphi_i^{(0)} |} = 0,$$

and a similar relation for the ket derivative. Evaluation of the second order functional derivatives  $\delta^2 \mathcal{E}_{\text{KS}}^{(0)} / \delta \langle \varphi_i^{(0)} | \delta \langle \varphi_j^{(0)} |$ ,  $\delta^2 \mathcal{E}_{\text{KS}}^{(0)} / \delta \langle \varphi_i^{(0)} | \delta | \varphi_j^{(0)} \rangle$  and  $\delta^2 \mathcal{E}_{\text{KS}}^{(0)} / \delta | \varphi_i^{(0)} \rangle \delta | \varphi_j^{(0)} \rangle$  produces a very complicated expression that simplifies considerably in the limit of orthogonal orbitals  $S_{ij} = \delta_{ij}$ . This leads to the expression,

$$\begin{aligned} \mathcal{E}^{(2)} = & \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' n^{(1)}(\mathbf{r}) K(\mathbf{r}, \mathbf{r}') n^{(1)}(\mathbf{r}') \\ & + \sum_{ij=1}^N \langle \varphi_i^{(1)} | (H_{\text{KS}}^{(0)} \delta_{ij} - \langle \varphi_j^{(0)} | H_{\text{KS}}^{(0)} | \varphi_i^{(0)} \rangle) | \varphi_j^{(1)} \rangle \\ & + \sum_{i=1}^N \left\langle \varphi_i^{(1)} \left| \frac{\delta \mathcal{E}_{\text{KS}}^{\text{pert}}}{\delta \langle \varphi_i^{(0)} |} + \frac{\delta \mathcal{E}_{\text{KS}}^{\text{pert}}}{\delta | \varphi_i^{(0)} \rangle} \right| \varphi_i^{(1)} \right\rangle, \end{aligned} \quad (9)$$

where

$$H_{\text{KS}} = -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}), \quad (10)$$

and

$$K(\mathbf{r}, \mathbf{r}') = \frac{\delta(V_H(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}))}{\delta n(\mathbf{r}')}, \quad (11)$$

supplemented by the orthogonality constraint which to first order on  $\lambda$  reads

$$\langle \varphi_i^{(0)} | \varphi_j^{(1)} \rangle + \langle \varphi_i^{(1)} | \varphi_j^{(0)} \rangle = 0, \quad \forall i, j. \quad (12)$$

For canonical orbitals:

$$\langle \varphi_j^{(0)} | H_{\text{KS}}^{(0)} | \varphi_i^{(0)} \rangle = \epsilon_i^{(0)} \delta_{ij}, \quad (13)$$

and Eq. (9) further simplifies to

$$\begin{aligned} \mathcal{E}^{(2)} = & \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' n^{(1)}(\mathbf{r}) K(\mathbf{r}, \mathbf{r}') n^{(1)}(\mathbf{r}') \\ & + \sum_{i=1}^N \langle \varphi_i^{(1)} | (H_{\text{KS}}^{(0)} - \epsilon_i^{(0)}) | \varphi_i^{(1)} \rangle \\ & + \sum_{i=1}^N \left\langle \varphi_i^{(1)} \left| \frac{\delta \mathcal{E}_{\text{KS}}^{\text{pert}}}{\delta \langle \varphi_i^{(0)} |} + \frac{\delta \mathcal{E}_{\text{KS}}^{\text{pert}}}{\delta | \varphi_i^{(0)} \rangle} \right| \varphi_i^{(1)} \right\rangle, \end{aligned} \quad (14)$$

which reduces to the form proposed by Gonze<sup>7</sup> if

$$\mathcal{E}_{\text{KS}}^{\text{pert}} = \sum_i \langle \varphi_i | h | \varphi_i \rangle. \quad (15)$$

### III. MINIMIZATION TECHNIQUES

As discussed in Ref. 7 in an appropriate choice of the gauge, we can replace Eq. (12) with the more stringent,

$$\langle \varphi_j^{(0)} | \varphi_i^{(1)} \rangle = 0 \quad \forall i, j, \quad (16)$$

which implies orthogonalizing the  $\{\varphi^{(1)}\}$  to the manifold of the  $\{\varphi^{(0)}\}$ . This constraint can be imposed via a Lagrange multiplier: to this effect we introduce the following Lagrangian:

$$\mathcal{L}^{(2)} = \mathcal{E}^{(2)} - \sum_{i,j} \langle \varphi_i^{(1)} | \varphi_j^{(0)} \rangle \Lambda_{ji}^{(1)}, \quad (17)$$

where  $\Lambda_{ij}^{(1)}$  is

$$\begin{aligned} \Lambda_{ij}^{(1)} = & \langle \varphi_i^{(1)} | (H^{(0)} - \epsilon_i^{(0)}) | \varphi_j^{(0)} \rangle + \langle \varphi_i^{(0)} | (H^{(0)} - \epsilon_j^{(0)}) | \varphi_j^{(1)} \rangle \\ & + \langle \varphi_i^{(0)} | \langle \varphi_j^{(0)} | K | \varphi_j^{(1)} \rangle + \langle \varphi_j^{(1)} | K | \varphi_j^{(0)} \rangle | \varphi_i^{(0)} \rangle \\ & + \left\langle \varphi_i^{(0)} \left| \frac{\delta \mathcal{E}_{\text{KS}}^{\text{pert}}}{\delta \langle \varphi_j^{(0)} |} + \frac{\delta \mathcal{E}_{\text{KS}}^{\text{pert}}}{\delta | \varphi_j^{(0)} \rangle} \right| \varphi_j^{(0)} \right\rangle. \end{aligned} \quad (18)$$

The minimum condition then yields the inhomogeneous nonlinear system for the  $\{\varphi^{(1)}\}$ :

$$\begin{aligned} -(H_{\text{KS}}^{(0)} - \epsilon_i^{(0)}) | \varphi_i^{(1)} \rangle = & \mathcal{P}^e \left( \int d^3 r' K(\mathbf{r}, \mathbf{r}') n^{(1)}(\mathbf{r}') | \varphi_i^{(0)} \rangle \right. \\ & \left. + \frac{\delta \mathcal{E}_{\text{KS}}^{\text{pert}}}{\delta | \varphi_j^{(0)} \rangle} \right), \end{aligned} \quad (19)$$

where

$$\mathcal{P}^e = 1 - \sum_j | \varphi_j^{(0)} \rangle \langle \varphi_j^{(0)} |. \quad (20)$$

Note that the right-hand side still depends on  $\{\varphi_i^{(1)}\}$  via the perturbation density  $n^{(1)}$ . The nonlinearity of Eq. (19) comes from the dependence of the right-hand side on  $n^{(1)}$ , and becomes more transparent if we note that

$$\int d\mathbf{r}' K(\mathbf{r}, \mathbf{r}') n^{(1)}(\mathbf{r}') = V_H^{(1)}(\mathbf{r}) + V_{xc}^{(1)}(\mathbf{r}), \quad (21)$$

where  $V_H^{(1)}$  and  $V_{xc}^{(1)}$  are the variations of the Hartree and exchange-correlation potentials induced by the change in the density. In terms of these two contributions Eq. (19) becomes

$$\begin{aligned} -(H_{\text{KS}}^{(0)} - \epsilon_i^{(0)}) | \varphi_i^{(1)} \rangle = & \mathcal{P}^e \left( V_H^{(1)}(\mathbf{r}) | \varphi_i^{(0)} \rangle + V_{xc}^{(1)}(\mathbf{r}) | \varphi_i^{(0)} \rangle \right. \\ & \left. + \frac{\delta \mathcal{E}_{\text{KS}}^{\text{pert}}}{\delta | \varphi_j^{(0)} \rangle} \right). \end{aligned} \quad (22)$$

Equations (17) and (22) are valid for canonical orbitals  $\{\varphi_i^{(0)}\}$ . In principle, they are also valid for other orbitals, e.g., for localized orbitals (Wannier functions). In that case, however, the full Hamiltonian matrix elements  $\langle \varphi_j^{(0)} | H_{\text{KS}}^{(0)} | \varphi_i^{(0)} \rangle$  must be used instead of the KS energies  $\epsilon_i^{(0)}$ .

### IV. EXCHANGE-CORRELATION FUNCTIONALS

The term  $V_{xc}^{(1)}$  is easily evaluated in the case of the local density approximation (LDA). However, its evaluation is more complex for GC functionals, which can be written in the form

$$\mathcal{E}_{xc} = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}[n(\mathbf{r}), \nabla_{\mathbf{r}} n(\mathbf{r})]. \quad (23)$$

The calculus of variations yields the following expression in terms of first and second derivatives of  $n^{(1)}$ :<sup>25</sup>

$$\begin{aligned} V_{xc}^{(1)}(\mathbf{r}) = & \frac{\partial^2 [n \varepsilon_{xc}(n, \nabla_{\mathbf{r}} n)]}{\partial n^2} \Big|_{n=n^{(0)}(\mathbf{r})} n^{(1)}(\mathbf{r}) - \sum_{\alpha} \frac{\partial}{\partial \mathbf{r}_{\alpha}} \left[ \frac{\partial^2 [n \varepsilon_{xc}(n, \nabla_{\mathbf{r}} n)]}{\partial n \partial (\partial_{\alpha} n)} \Big|_{n=n^{(0)}(\mathbf{r})} \right] n^{(1)}(\mathbf{r}) \\ & - \sum_{\alpha, \beta} \frac{\partial}{\partial \mathbf{r}_{\alpha}} \left[ \frac{\partial^2 [n \varepsilon_{xc}(n, \nabla_{\mathbf{r}} n)]}{\partial (\partial_{\alpha} n) \partial (\partial_{\beta} n)} \Big|_{n=n^{(0)}(\mathbf{r})} \right] \frac{\partial n^{(1)}(\mathbf{r})}{\partial \mathbf{r}_{\beta}} - \sum_{\alpha, \beta} \left[ \frac{\partial^2 [n \varepsilon_{xc}(n, \nabla_{\mathbf{r}} n)]}{\partial (\partial_{\alpha} n) \partial (\partial_{\beta} n)} \Big|_{n=n^{(0)}(\mathbf{r})} \right] \frac{\partial^2 n^{(1)}(\mathbf{r})}{\partial \mathbf{r}_{\alpha} \partial \mathbf{r}_{\beta}}. \end{aligned} \quad (24)$$

The evaluation of these terms is rather cumbersome. In addition, the derivatives lead to large inverse powers of the density. When the density becomes small these terms are a source of numerical noise. One could ignore the contribution to  $E_{xc}^{\text{GC}}$  for densities smaller than a preassigned value as is done in practice for the first order derivative. However the large negative powers that appear in the second derivative need to be cured with a much too high cut-off density value. This induces inaccuracies and numerical noise. We resort instead to a finite difference technique. For this effect we observe that

$$\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' n^{(1)}(\mathbf{r}') \frac{\delta^2 \mathcal{E}_{xc}}{\delta n^{(0)}(\mathbf{r}') \delta n^{(0)}(\mathbf{r})} n^{(1)}(\mathbf{r}) = \frac{1}{2} \lim_{\varepsilon \rightarrow 0} \frac{\mathcal{E}_{xc}[n^{(0)}(\mathbf{r}) + \varepsilon n^{(1)}(\mathbf{r})] + \mathcal{E}_{xc}[n^{(0)}(\mathbf{r}) - \varepsilon n^{(1)}(\mathbf{r})] - 2\mathcal{E}_{xc}[n^{(0)}(\mathbf{r})]}{\varepsilon^2}, \quad (25)$$

and therefore

$$V_{xc}^{(1)} = \lim_{\varepsilon \rightarrow 0} \frac{V_{xc}(n^{(0)}(\mathbf{r}) + \varepsilon n^{(1)}(\mathbf{r})) - V_{xc}(n^{(0)}(\mathbf{r}) - \varepsilon n^{(1)}(\mathbf{r}))}{2\varepsilon}. \quad (26)$$

In Eq. (26), accuracy requires the use of a small  $\varepsilon$ , but on the other hand, numerical stability favors a large  $\varepsilon$ . After some experimentation, we find that a good compromise can be achieved with a value of  $\varepsilon \approx 10^{-3}$ .

Our numerical approach is more reliable and stable than the analytical expression. In a PW approach, our way of proceeding is also computationally cheaper: in fact in Eq. (24) one needs to evaluate  $\partial n^{(1)}/\partial \mathbf{r}_\alpha$  and  $\partial^2 n^{(1)}/\partial \mathbf{r}_\alpha \partial \mathbf{r}_\beta$ , which require a total of nine fast Fourier transforms compared with the six fast Fourier transforms of Eq. (26), not to mention the cost of evaluating the very complex functions in Eq. (24).

## V. VIBRATIONAL MODES

We now turn to some illustrative examples of our method. We start with the calculation of the vibrational modes. This can be achieved by diagonalizing the dynamical matrix,

$$D_{\alpha i \beta j} = \frac{1}{\sqrt{m_\alpha m_\beta}} \left( \frac{\partial^2 E_{I-e}}{\partial R_{\alpha i} \partial R_{\beta j}} + \frac{\partial^2 E_{KS}}{\partial R_{\alpha i} \partial R_{\beta j}} \right), \quad (27)$$

where we indicate the ions with Greek indices  $\alpha = 1, N_I$  ( $N_I$  is the number of ions) and the Cartesian coordinates with Latin indices  $i = 1, 2, 3$ . The first term in this matrix can be calculated from the direct derivative of the ionic repulsion potential. The second term comes from the interaction of the electrons with the nuclei and we will show here in Sec. V how it can be calculated using the methods presented earlier. In this case we consider  $3N_I$  perturbations, one for each small displacement  $u_{\alpha i}$  of the atom  $\alpha$  from its equilibrium position  $\mathbf{R}_\alpha$  in the direction  $i$ . The perturbative functional is given by

$$\mathcal{E}^{\text{pert}}[n] = \int d^3r n(\mathbf{r}) \sum_{\beta=1, N_I} \frac{\partial V_{I-e}(\mathbf{r}-\mathbf{R}_\beta)}{\partial R_{\alpha i}} \delta_{\alpha\beta}, \quad (28)$$

where  $V_{I-e}$  describes the ionic Coulomb potential. In the PW approach one uses instead norm-conserving pseudopotentials.<sup>14</sup> Present day applications use mostly non-local potentials of separable form,<sup>15</sup> which are computationally very convenient,

$$V_{I-e} = v_{\text{loc}} + \sum_{l=1}^{l_{\text{max}}} |p_l\rangle \omega_l \langle p_l|, \quad (29)$$

where  $v_{\text{loc}}$  is a local operator,  $p_l$  the projector on the  $l$  angular moment and  $\omega_l$  appropriate weights. Using Eq. (29) the perturbation functional reads

$$\begin{aligned} \mathcal{E}^{\text{pert}}[n] &= \int d^3r n(\mathbf{r}) \sum_{\beta=1}^{N_I} \frac{\partial v_{\text{loc}}(\mathbf{r}-\mathbf{R}_\beta)}{\partial R_{\alpha i}} \delta_{\alpha\beta} \\ &+ \sum_{l=1}^{l_{\text{max}}} \sum_{\beta=1}^{N_I} \sum_k \left( \left\langle \varphi_k \left| \frac{\partial p_l(r-\widehat{R}_\beta)}{\partial R_{\alpha i}} \right| \right\rangle \omega_l \langle p_l(r-\widehat{R}_\beta) | \varphi_k \rangle \right. \\ &\left. + \langle \varphi_k | p_l(r-\widehat{R}_\beta) \rangle \omega_l \left\langle \frac{\partial p_l(r-\widehat{R}_\beta)}{\partial R_{\alpha i}} \right| \varphi_k \right) \delta_{\alpha\beta}, \quad (30) \end{aligned}$$

and the perturbative term in Eq. (14) becomes

$$\begin{aligned} &\int d^3r n^{(1)}(\mathbf{r}) \sum_{\beta=1}^{N_I} \frac{\partial v_{\text{loc}}(\mathbf{r}-\mathbf{R}_\beta)}{\partial R_{\alpha i}} \delta_{\alpha\beta} \\ &+ \sum_l \sum_\beta \sum_k \left( \left\langle \varphi_k^{(1)} \left| \frac{\partial p_l}{\partial R_{\alpha i}} \right| \right\rangle \omega_l \langle p_l | \varphi_k^{(0)} \rangle \right. \\ &+ \langle \varphi_k^{(0)} | p_l \rangle \omega_l \left\langle \frac{\partial p_l}{\partial R_{\alpha i}} \right| \varphi_k^{(1)} \rangle \left\langle \varphi_k^{(0)} \left| \frac{\partial p_l}{\partial R_{\alpha i}} \right| \right\rangle \psi_l \langle p_l | \varphi_k^{(1)} \rangle \\ &\left. + \langle \varphi_k^{(1)} | p_l \rangle \omega_l \left\langle \frac{\partial p_l}{\partial R_{\alpha i}} \right| \varphi_k^{(0)} \right\rangle \right) \delta_{\alpha\beta}. \quad (31) \end{aligned}$$

The electronic term can be calculated using the Hellmann–Feynman theorem generalized to the nonlocal potential:

$$\frac{\partial E_{KS}}{\partial R_{\alpha i}} = \sum_k \left\langle \varphi_k^{(0)} \left| \frac{\partial V_{I-e}}{\partial R_{\alpha i}} \right| \varphi_k^{(0)} \right\rangle, \quad (32)$$

and taking the second derivative,

$$\begin{aligned} \frac{\partial^2 E_{KS}}{\partial R_{\alpha i} \partial R_{\beta j}} &= \sum_k \left\langle \varphi_k^{(0)} \left| \frac{\partial^2 V_{I-e}}{\partial R_{\alpha i} \partial R_{\beta j}} \right| \varphi_k^{(0)} \right\rangle + \left\langle \varphi_{k,\alpha i}^{(1)} \left| \frac{\partial V_{I-e}}{\partial R_{\beta j}} \right| \varphi_k^{(0)} \right\rangle + \left\langle \varphi_k^{(0)} \left| \frac{\partial V_{I-e}}{\partial R_{\beta j}} \right| \varphi_{k,\alpha i}^{(1)} \right\rangle \\ &= \sum_k \left( \left\langle \varphi_k^{(0)} \left| \frac{\partial^2 v_{\text{loc}}}{\partial R_{\alpha i} \partial R_{\beta j}} \right| \varphi_k^{(0)} \right\rangle + \sum_l \left\langle \varphi_k^{(0)} \left| \frac{\partial^2 p_l}{\partial R_{\alpha i} \partial R_{\beta j}} \right| \right\rangle \omega_l \langle p_l | \varphi_k^{(0)} \rangle + \langle \varphi_k^{(0)} | p_l \rangle \omega_l \left\langle \frac{\partial^2 p_l}{\partial R_{\alpha i} \partial R_{\beta j}} \right| \varphi_k^{(0)} \right\rangle \\ &+ 2 \left\langle \varphi_k^{(0)} \left| \frac{\partial p_l}{\partial R_{\alpha i}} \right| \right\rangle \omega_l \left\langle \frac{\partial p_l}{\partial R_{\beta j}} \right| \varphi_k^{(0)} \right\rangle \delta_{\alpha\beta} + \left\langle \varphi_{k,\alpha i}^{(1)} \left| \frac{\partial v_{\text{loc}}}{\partial R_{\beta j}} \right| \varphi_k^{(0)} \right\rangle + \left\langle \varphi_k^{(0)} \left| \frac{\partial v_{\text{loc}}}{\partial R_{\beta j}} \right| \varphi_{k,\alpha i}^{(1)} \right\rangle + \sum_l \left\langle \varphi_{k,\alpha i}^{(1)} \left| \frac{\partial p_l}{\partial R_{\beta j}} \right| \right\rangle \omega_l \langle p_l | \varphi_k^{(0)} \rangle \\ &+ \langle \varphi_{k,\alpha i}^{(1)} | p_l \rangle \omega_l \left\langle \frac{\partial p_l}{\partial R_{\beta j}} \right| \varphi_k^{(0)} \right\rangle + \left\langle \varphi_k^{(0)} \left| \frac{\partial p_l}{\partial R_{\beta j}} \right| \right\rangle \omega_l \langle p_l | \varphi_{k,\alpha i}^{(1)} \rangle + \langle \varphi_k^{(0)} | p_l \rangle \omega_l \left\langle \frac{\partial p_l}{\partial R_{\beta j}} \right| \varphi_{k,\alpha i}^{(1)} \right\rangle. \quad (33) \end{aligned}$$



We applied the method to isolated molecules. In particular, we report in Tables I and II the results for the molecules of disilane ( $\text{Si}_2\text{H}_6$ ) and formaldehyde ( $\text{CH}_2\text{O}$ ) in the LDA approximation. In the case of disilane we used a cubic cell with a reticular constant of 22 a.u., Martins–Trouiller pseudopotentials<sup>16</sup> and a PW cutoff of 50 Ry. In the case of formaldehyde we used a cubic cell with a reticular constant of 24 a.u., Martins–Trouiller pseudopotentials<sup>16</sup> and a PW cutoff of 70 Ry. We performed our calculations using the Car–Parrinello molecular dynamics (CPMD) code,<sup>17</sup> into which we have implemented the method presented here. We compare our results with the ones obtained by finite differences using CPMD with the same cell, cutoff and pseudopotentials and we find very good agreement, which validates our approach. For comparison we report calculation made using the GAUSSIAN program,<sup>18</sup> which is an all-electron method and which expands the KS orbitals into Gaussians. We also show as a reference the experimentally determined frequencies which are in good agreement with all the theoretical results. (The experimental frequencies reported are the observed fundamentals.<sup>19</sup>)

## VI. RAMAN SPECTRA

As discussed in Sec. I, a case in which the perturbation cannot be expressed in a Hamiltonian form is that of an external electric field, which couples with the electric polarization  $\mathbf{P}^{\text{ele}} = e\langle \mathbf{r} \rangle$  in a periodic system. The latter, using the modern theory of polarization in the  $\Gamma$  only sampling of the Brillouin zone, can be written in terms of Berry phase  $\gamma_\mu$ :<sup>9</sup>

$$\gamma_\mu = \text{Im} \log \det \mathbf{Q}^{(\mu)}, \quad (34)$$

where the matrix  $\mathbf{Q}^{(\mu)}$  is defined as  $\mathbf{Q}_{i,j}^{(\mu)} = \langle \varphi_i | e^{i\mathbf{G}_\mu \cdot \mathbf{r}} | \varphi_j \rangle$ , and  $\mathbf{G}_\mu$  is the smallest vector in a periodically repeated cubic cell in direction  $\mu$ . Equation (34) can be generalized to cells

TABLE I. Vibrational modes of disilane: Comparison between perturbation theory (PT), finited differences (FD), the Gaussian code [6–311G<sup>†</sup>(3df,3pd) basis set] and experiments (Ref. 20). For PT and FD we used a cubic cell with a reticular constant of 22 a.u., Martins–Trouiller pseudopotentials, the LDA approximation and a PW cutoff of 50 Ry. The frequencies are in  $\text{cm}^{-1}$ .

	PT	FD	6–311G <sup>†</sup> (3df,3pd)	Experiment
$E_u$	2153	2153	2187	2177
$A_{1g}$	2152.88	2152.88	2186	2163
$A_{2u}$	2144	2144	2177	2154
	2143	2143	2177	
$E_g$	2132	2132	2166	2153
	2128	2128	2162	
$E_u$	897	897	902	946
	896	896	902	
$E_g$	883	883	889	929
	883	883	889	
$A_{1g}$	846	846	850	910
$A_{2u}$	775	775	781	843
$E_g$	595	595	595	625
	593	593	594	
$A_{1g}$	428	428	433	434
$E_u$	337	337	338	379
	334	334	338	
$A_{1u}$	134	134	143	180

of arbitrary shape.<sup>22</sup> This formula is in principle valid with in the limit of an infinite dimension of the cell, but in a non-conducting material this is a good approximation even with relatively small supercells.  $\mathbf{P}_\mu^{\text{ele}}$  is then given by

$$\mathbf{P}_\mu^{\text{ele}} = \frac{2|e|}{|\mathbf{G}_\mu|} \gamma_\mu. \quad (35)$$

This induces a perturbation in the KS functional of the type

$$\begin{aligned} \lambda \mathcal{E}_{\text{KS}}^{\text{pert}}[\{\varphi_i\}] &= -\mathbf{E} \cdot \mathbf{P}^{\text{ele}} \\ &= -\sum_\nu E_\nu \frac{2|e|}{|\mathbf{G}_\nu|} \text{Im} \log \det \langle \varphi_i | e^{i\mathbf{G}_\nu \cdot \mathbf{r}} | \varphi_j \rangle. \end{aligned} \quad (36)$$

In this case the perturbative parameter is  $E_\nu$  and  $|\varphi_i\rangle \simeq |\varphi_i^{(0)}\rangle - E_\nu |\varphi_i^{(1)}\rangle$ . The derivative  $\delta \mathcal{E}_{\text{KS}}^{\text{pert}} / \delta \langle \varphi_i^{(0)} |$  and its ket conjugate can be evaluated using the formula for the derivative of a matrix  $A$  with respect to a generic variable  $x$ :

$$\frac{d}{dx} \ln \det A = \text{Tr} \frac{dA_{ij}}{dx} A_{ji}^{-1}. \quad (37)$$

The perturbative term in Eq. (9) becomes

$$\begin{aligned} \frac{2|e|}{|\mathbf{G}_\nu|} \text{Im} \left[ \sum_{i,j} \langle \varphi_i^{(1)} | e^{i\mathbf{G}_\nu \cdot \mathbf{r}} | \varphi_j^{(0)} \rangle \right. \\ \left. + \langle \varphi_i^{(0)} | e^{i\mathbf{G}_\nu \cdot \mathbf{r}} | \varphi_j^{(1)} \rangle \mathbf{Q}_{j,i}^{(\nu)-1} \right]. \end{aligned} \quad (38)$$

Using this perturbative term in Eq. (9) we can calculate, solving the nonlinear system of Eq. (22), the first order correction to the wave functions  $\{\varphi_i^{(1)}\}$ . This allows us to evaluate the induced dipole moment in the  $\mu$  direction to linear terms:

$$\begin{aligned} \delta P_\mu^{\text{ele}} &= \frac{2|e|}{|\mathbf{G}_\mu|} \delta \gamma_\mu \\ &= -\sum_\nu \frac{2|e|}{|\mathbf{G}_\nu|} \text{Im} \left[ \sum_{i,j} \langle \varphi_i^{(1)} | e^{i\mathbf{G}_\mu \cdot \mathbf{r}} | \varphi_j^{(0)} \rangle \right. \\ &\quad \left. + \langle \varphi_i^{(0)} | e^{i\mathbf{G}_\mu \cdot \mathbf{r}} | \varphi_j^{(1)} \rangle \mathbf{Q}_{j,i}^{(\nu)-1} \right] E_\nu, \end{aligned} \quad (39)$$

and the polarizability  $\alpha_{\mu\nu} = -\partial P_\mu / \partial E_\nu$ :

TABLE II. Vibrational modes of formaldehyde: Comparison between perturbation theory (PT), finited differences (FD), the Gaussian code [6–311G<sup>†</sup>(3df,3pd) and 6–311G basis sets] and experiments (Ref. 21). For PT and FD we used a cubic cell with a reticular constant of 24 a.u., Martins–Trouiller pseudopotentials, the LDA approximation and a PW cutoff of 70 Ry. The frequencies are in  $\text{cm}^{-1}$ .

	PT	FD	6–311G <sup>†</sup> (3df,3pd)	6–311G	Experiment
$b_2$	2828	2828	2850	2898	2874
$a_1$	2776	2776	2796	2832	2780
$a_1$	1809	1809	1818	1720	1743.6
$a_1$	1458	1458	1466	1516	1503
$b_2$	1214	1214	1217	1248	1280
$b_1$	1138	1138	1146	1177	1167

TABLE III. Polarizability of a molecule of water as a function of the length  $L$  of the cubic cell. We used Martins–Trouiller pseudopotentials, the *BLYP* gradient corrections functional and a PW cutoff of 70 Ry:

$L$ (a.u.)	$\alpha_1$	$\alpha_2$ $\text{\AA}^3$	$\alpha_3$
15	1.46	1.36	1.27
25	1.57	1.51	1.47
35	1.61	1.57	1.53
45	1.63	1.59	1.57
Ref. 23	1.62	1.60	1.59

$$\alpha_{\mu,v} = \frac{2|e|}{|\mathbf{G}_\mu|} \text{Im} \left[ \sum_{ij} \langle \varphi_i^{v(1)} | e^{i\mathbf{G}_\mu \cdot \mathbf{r}} | \varphi_j^{(0)} \rangle + \langle \varphi_i^{(0)} | e^{i\mathbf{G}_\mu \cdot \mathbf{r}} | \varphi_j^{v(1)} \rangle \right] \mathbf{Q}_{j,i}^{(v)-1}. \quad (40)$$

In order to find the minimum of Eq. (14) we use a preconditioned conjugated gradient approach (see Appendix A) which gave a converged result of the order of  $\approx 15$  iterations.

We tested the validity of this approach by performing a set of calculations on isolated molecules which we treat within the supercell scheme. In order to evaluate the effect of the finite dimension of the cell, we performed several calculations with different sized cells and we extrapolated the value of the polarizability for an infinite cell. We report the results of this study in the case of a molecule of water in Table III. We have compared our results with standard quantum chemical calculations. The agreement was excellent especially if one takes into account the difference between the two calculations (different basis set, use of the pseudopotential in our case, etc.).

We applied the present scheme to a truly periodic system, in which the use of the Berry phase approach is mandatory. Here the comparison is less straightforward since one needs to perform adequate sampling over the Brillouin zone (BZ). The present implementation is restricted to the  $\Gamma$  point only of the BZ and therefore BZ sampling convergence studies have to be replaced with calculations on larger and larger supercells. In particular we treat the case of silicon and we compare it with the results of Baroni and Resta.<sup>24</sup> First we evaluated the dielectric constant  $\epsilon_\infty$ ,

$$\epsilon_\infty = 1 + 4\pi \frac{\partial \mathbf{P}}{\partial \mathbf{E}}, \quad (41)$$

and we compared our results with the results of Dal Corso *et al.*<sup>25</sup> As one can see from Table IV the convergence of such a quantity with the number of atoms in the cell is quite slow. Because we are interested in Raman spectrum calculations, we performed a more stringent test, evaluating by a finite difference method, the derivative of the polarizability with respect to the atomic displacements from the equilibrium  $\gamma$ , which is the quantity that really determines the Raman activity.

The latter converges much faster. In fact we calculate the value of the derivatives of the polarizability in the direction (1, 1, 1) for different values of a dimensionless amplitude  $u$  moving the atomic positions of  $\pm ua(1,1,1)$  where  $a$  is the

TABLE IV. Dielectric constant of silicon: We performed several calculations of  $\epsilon_\infty$  as a function of the number of atoms in the cell. We used PW, Car–von Barth pseudopotential and the LDA approximation. The cutoff was of 14 Ry.

$N$	8	64	216	Ref. 25
$\epsilon_\infty$	6.6	8.58	9.81	12.9

lattice constant. The results for  $\gamma(u)/u$ , reported in Table V, are in good agreement with Ref. 24 and show that these derivatives converge to a limit value independent of the size of the cell.

## VII. NUCLEAR MAGNETIC RESONANCE

One of the most powerful tools used in chemistry to determine the chemical structure of crystals and molecules is the measurement of the chemical shift tensor or, more frequently, its trace (isotropic shift).

The chemical shift  $\sigma_I = \sigma(\mathbf{R}_I)$  is a second order property: the measured quantity is derived from the energy term bilinear in the external magnetic field  $\mathbf{B}^e$  and the nuclear magnetic moment. The magnetic susceptibility instead corresponds to the energy term quadratic in the external field. The common perturbation Hamiltonian for shifts and susceptibilities is

$$h = \frac{e}{m} \mathbf{p} \cdot \mathbf{A}(\mathbf{r}) + \frac{e^2}{2m} \mathbf{A}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}), \quad (42)$$

with a vector potential  $\mathbf{A}$  defined through  $\mathbf{B}^e = \nabla \times \mathbf{A}(\mathbf{r})$ . A suitable vector potential for a homogeneous magnetic field  $\mathbf{B}^e$  is

$$\mathbf{A}(\mathbf{r}) = -\frac{1}{2}(\mathbf{r} - \mathbf{R}^O) \times \mathbf{B}^e,$$

with an arbitrary gauge origin  $\mathbf{R}^O$ . This leads to a second order perturbation functional,

$$\begin{aligned} \mathcal{E}^{\text{pert}} &= \sum_k \langle \varphi_k | h | \varphi_k \rangle \\ &= \sum_k \frac{e^2}{2m} \langle \varphi_k^{(0)} | \mathbf{A}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) | \varphi_k^{(0)} \rangle \\ &\quad + \frac{e}{m} \langle \langle \varphi_k^{(1)} | \mathbf{p} \cdot \mathbf{A}(\mathbf{r}) | \varphi_k^{(0)} \rangle + \langle \varphi_k^{(0)} | \mathbf{p} \cdot \mathbf{A}(\mathbf{r}) | \varphi_k^{(1)} \rangle \rangle. \end{aligned} \quad (43)$$

Using this functional, the electronic response can be computed in terms of the perturbation wave functions  $\varphi_i^{(1)}$ . With the help of these, the induced current reads

TABLE V.  $\gamma(u)/u$  for silicon: Comparison with the previous results of Baroni and Resta (Ref. 24). We present the data for  $u=0.0001$ .

$N$	8	64	Ref. 24	Experiment
$\gamma(u)/u$	6	6	7.15	$6.2 \pm 1$

$$\begin{aligned} \mathbf{j}(\mathbf{r}) = & \frac{e}{m} \mathbf{A}(\mathbf{r}) \sum_i |\varphi_i^{(0)}(\mathbf{r})|^2 \\ & + \frac{1}{2m} \sum_i \langle \varphi_i^{(0)} | [\mathbf{p}|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|\mathbf{p}] | \varphi_i^{(1)} \rangle \\ & + \langle \varphi_i^{(1)} | [\mathbf{p}|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|\mathbf{p}] | \varphi_i^{(0)} \rangle. \end{aligned} \quad (44)$$

The two terms in Eq. (44) have large absolute values with opposite sign, leading to an important cancellation error. Their relative magnitude depends strongly on the choice of the gauge  $\mathbf{R}^{(0)}$ .

Several methods have been developed to minimize the numerical errors due to this cancellation.<sup>26–28,30</sup> They all choose particular values of the gauge in order to decrease the absolute magnitude of the two current contributions.

One particular choice to reduce this problem is the individual gauges for localized orbitals (IGLO) method.<sup>11</sup> This variant transforms the canonical wave functions  $|\varphi_k^{(0)}\rangle$  to maximally localized orbitals and uses their center of charge for the gauge origin,  $\mathbf{R}^O = \mathbf{R}_k^O$ . This is achieved by rewriting the variational expression for the total energy, Eq. (14), in terms of gauge-transformed wave functions,

$$|\tilde{\varphi}_k\rangle = e^{-i\Lambda_k} |\varphi_k\rangle.$$

The corresponding transformation  $\Lambda_k$  is given by

$$\Lambda_k = -\frac{1}{2} \mathbf{B} \cdot (\mathbf{r} \times \mathbf{R}_k^O).$$

The expansion to second order in  $\mathbf{B}$  yields a new perturbation functional,

$$\begin{aligned} \mathcal{E}^{\text{pert}} = & \sum_k \frac{e^2}{2m} \langle \tilde{\varphi}_k^{(0)} | \tilde{\mathbf{A}}_k(\mathbf{r}) \cdot \tilde{\mathbf{A}}_k(\mathbf{r}) | \tilde{\varphi}_k^{(0)} \rangle \\ & + \frac{e}{m} \langle \langle \tilde{\varphi}_k^{(1)} | \mathbf{p} \cdot \tilde{\mathbf{A}}_k(\mathbf{r}) | \tilde{\varphi}_k^{(0)} \rangle + \langle \tilde{\varphi}_k^{(0)} | \mathbf{p} \cdot \tilde{\mathbf{A}}_k(\mathbf{r}) | \tilde{\varphi}_k^{(1)} \rangle \rangle \\ & + \sum_{kl} i \langle \tilde{\varphi}_k^{(1)} | \Lambda_k - \Lambda_l | \tilde{\varphi}_l^{(0)} \rangle \langle \tilde{\varphi}_l^{(0)} | H^{(0)} | \tilde{\varphi}_k^{(0)} \rangle. \end{aligned} \quad (45)$$

Here, the transformed vector potential  $\tilde{\mathbf{A}}_k(\mathbf{r})$  reads simply

$$\tilde{\mathbf{A}}_k(\mathbf{r}) = -\frac{1}{2} (\mathbf{r} - \mathbf{R}_k^O) \times \mathbf{B}^e. \quad (46)$$

With this perturbation functional using localized orbitals with individual gauges, the second order energy, Eq. (14), becomes variational in the  $\tilde{\varphi}_k^{(1)}$ . The orthogonality relation, Eq. (12), however, must be slightly modified for the new orbitals:

$$\langle \tilde{\varphi}_k^{(0)} | \tilde{\varphi}_j^{(1)} \rangle = \langle \tilde{\varphi}_k^{(0)} | \Lambda_k | \tilde{\varphi}_j^{(0)} \rangle, \quad \forall k, j.$$

Finally, the vector potential  $\mathbf{A}(\mathbf{r})$  in the current expression, Eq. (44), must be transformed into the new individual gauges  $\mathbf{R}_k^O$ , yielding the same  $\tilde{\mathbf{A}}_k(\mathbf{r})$  as that of Eq. (46).

However, the principle remains unchanged and one can obtain first order perturbation wave functions, now for localized orbitals, with the algorithm described earlier. Then the electronic current is calculated by Eq. (44), which leads to the induced magnetic field that determines the chemical shifts.

TABLE VI. Absolute isotropic NMR chemical shifts (in ppm) obtained using experimental geometries. The pseudopotential was of Stefan–Goedecker type (Ref. 32), the wave functions were expanded in plane waves up to a cut-off energy of 120 Ry in a cubic cell with a box length of 20 a.u. and we used the *BLYP* gradient corrections. The values from GAUSSIAN (Ref. 18) were obtained with a 6–311G(3df,3pd) basis set.

	$\sigma^{Ha}$	$\sigma^{Hb}$	$\sigma_{\text{exp}}^{Hc}$	$\sigma^{Ca}$	$\sigma^{Cb}$	$\sigma^{Cc}$
C <sub>2</sub> H <sub>2</sub>	30.2	31.0	29.26	127	115.0	117.2
C <sub>2</sub> H <sub>4</sub>	25.5	25.3	25.43	79	52.6	64.5
C <sub>2</sub> H <sub>6</sub>	29.8	30.4	29.86	174	174.5	180.9
C <sub>6</sub> H <sub>6</sub>	24.1	23.8	23.70	78	53.3	57.2
CH <sub>4</sub>	30.7	31.1	30.60	187	189.1	195.1

<sup>a</sup>This work

<sup>b</sup>Reference 18.

<sup>c</sup>Reference 31.

The use of pseudopotentials is somewhat problematic, since the orbitals have a nonphysical shape in the vicinity of the nuclei, where their interaction with the nuclear spin is strongest. However, it has been shown<sup>29</sup> that for many nuclei the correction with an additive constant compensates very well for this deficiency. The contribution from the core electrons is almost independent of the chemical environment of the atom.<sup>11</sup>

Computed values for the NMR chemical shift of a representative set of small organic molecules are shown in Table VI. They have been obtained using experimental geometries. The pseudopotential was of Stefan–Goedecker type,<sup>32</sup> the wave functions were expanded in plane waves up to a cut-off energy of 120 Ryd in a cubic cell with a box length of 20 a.u. and we used *BLYP* gradient corrections. The values from GAUSSIAN<sup>18</sup> were obtained with a 6–311G(3df,3pd) basis set.

The agreement with experiment is excellent for the hydrogen shifts and still good for the carbon nuclei. For hydrogen, no additional constant is needed to compensate for the pseudopotential, as there are no core electrons. This results in quantitative agreement with the GAUSSIAN implementation as well as with experiment. Instead, the carbon shifts are corrected for the 1s core electrons with an additive constant of 130 ppm. This value is empirical and depends on the coordination of the carbon. With our value, the shift is slightly underestimated in the absence  $\pi$ -type orbitals and somewhat overestimated in their presence. In similar chemical environments, however, the relative shifts are also in quantitative agreement with both GAUSSIAN implementation and experiments.

## VIII. CONCLUSION

We have shown in this article that variational perturbation theory in the framework of DFT can be generalized to perturbations that cannot be described in terms of a Hamiltonian. In order to further validate our theory, we performed several tests on different kinds of perturbations (vibrational modes, polarizability, and NMR chemical shifts). The results are in very good agreement with previous calculations and experimental results. In combination with the CPMD code, this module will provide a useful and versatile tool by which



to investigate the properties described above as well as other important quantities like chemical hard- and softness, elastic constants, etc.

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## APPENDIX A: PRECONDITIONING

In advanced optimization algorithms such as conjugate gradient minimization or direct inversion of iterative subspace (DIIS), good preconditioning is a key ingredient for optimal performance. The main objective is to reduce the condition number of the problem. In terms of the energy functional, Eq. (14), to be minimized, this is equivalent to finding a good inverse of

$$H^{(0)}\delta_{ij} - \langle \varphi_i^{(0)} | H^{(0)} | \varphi_j^{(0)} \rangle. \quad (\text{A1})$$

In order to obtain a reasonably simple and numerically reliable expression, we first replace the matrix elements,  $\langle \varphi_i^{(0)} | H^{(0)} | \varphi_j^{(0)} \rangle$  by the trace of the Hamiltonian,

$$\langle \varphi_i^{(0)} | H^{(0)} | \varphi_j^{(0)} \rangle \mapsto \delta_{ij} \frac{1}{N} \sum_k \langle \varphi_k^{(0)} | H^{(0)} | \varphi_k^{(0)} \rangle,$$

such that our operator, Eq. (A1), becomes unique for all orbitals.

In addition, we note that, since our implementation uses plane waves, the dominant contributions for high  $\mathbf{G}$  come from the kinetic energy term that in this representation is diagonal. We thus approximate Eq. (A1) by its  $(\mathbf{G}, \mathbf{G})$  elements. The resulting expression is

$$\frac{1}{2} |\mathbf{G}|^2 + V(\mathbf{G}) - \frac{1}{N} \text{Tr} H^{(0)}, \quad (\text{A2})$$

which can easily be inverted to obtain the preconditioning matrix. However, Eq. (A2) can become very small and may almost vanish for certain  $\mathbf{G}$  vectors. To prevent the preconditioner from being singular, we smoothly keep Eq. (A2) above a certain value  $\eta$  by transforming it to

$$\left[ \left( \frac{1}{2} |\mathbf{G}|^2 + V(\mathbf{G}) - \frac{1}{N} \text{Tr} H^{(0)} \right)^2 + \eta^2 \right]^{1/2},$$

or, optionally, to an alternative variant,

$$\frac{\left( \frac{1}{2} |\mathbf{G}|^2 + V(\mathbf{G}) - \frac{1}{N} \text{Tr} H^{(0)} \right)^2 + \eta^2}{\frac{1}{2} |\mathbf{G}|^2 + V(\mathbf{G}) - \frac{1}{N} \text{Tr} H^{(0)}},$$

which preserves changes in the sign of Eq. (A2).

In this way, our expression is never smaller than  $\eta$  and can safely be inverted. The final preconditioner then yields

$$\left[ \left( \frac{1}{2} |\mathbf{G}|^2 + V(\mathbf{G}) - \frac{1}{N} \text{Tr} H^{(0)} \right)^2 + \eta^2 \right]^{-1/2} \delta_{ij},$$

or, alternatively,

$$\frac{\frac{1}{2} |\mathbf{G}|^2 + V(\mathbf{G}) - \frac{1}{N} \text{Tr} H^{(0)}}{\left( \frac{1}{2} |\mathbf{G}|^2 + V(\mathbf{G}) - \frac{1}{N} \text{Tr} H^{(0)} \right)^2 + \eta^2} \delta_{ij}.$$

With these preconditioners and an appropriate value of  $\eta$ , the number of iterations needed to minimize the second order energy functional is approximately three times less than without preconditioning.

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