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Density-functional perturbational theory for dielectric tensors in the ultrasoft pseudopotential scheme

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We introduce a density-functional perturbational scheme based on ultrasoft pseudopotentials for calculating dielectric tensors of periodic systems. We obtain a variational functional for the second-order derivative of the energy with respect to an electric field. Our scheme makes use of the correspondence between all-electron and pseudo-wave-functions introduced in the projector augmented wave method. While we here specifically focus on ultrasoft pseudopotentials, our scheme also covers the case of norm-conserving ones. In the latter case, our formulation coincides with earlier ones but highlights the implied approximations. By construction, our scheme also applies to the all-electron projector augmented wave method. We first assess the validity of our scheme by calculating polarizability tensors and Raman intensities of small molecules (H_2O, CH_4, NH_3). We find good agreement with both experimental data and previous all-electron results. We then illustrate the potential of our scheme for treating systems of relatively large size through an application to a disordered model structure of vitreous silica.

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I. INTRODUCTION

Electronic structure calculations within density-functional theory based on plane-wave basis sets and pseudopotentials have grown into a widespread tool for investigating the properties of extended materials. The use of plane waves offers important advantages, such as a uniform sampling of space, atom-independent basis functions, and theoretical simplicity.[1] However, the computational effort to describe systems with localized states, such as first-row elements or transition metals, has often been prohibitive due to the large amount of required basis functions.

In the early 1990s, the development of ultrasoft pseudopotentials[2] and their implementation in standard density-functional calculations[1] have opened the way to the treatment of almost any element of the periodic table at an affordable computational cost. In the ultrasoft pseudopotential scheme, the electronic charge density is augmented in the core regions, thereby allowing for smoother electronic wave functions. This benefit is achieved at the cost of introducing generalized orthonormality constraints which depend on the ionic positions. The continued success of the ultrasoft pseudopotential scheme is further demonstrated by the availability of this scheme in a large set of current computational packages.[1,3–7]

The ultrasoft pseudopotential scheme shows important similarities with the projector augmented wave method.[8] Indeed, the relationship between all-electron and pseudo-wave-functions introduced in the latter method also applies to the ultrasoft pseudopotential scheme.[9] In particular, this relationship allows one to express expectation values of observables for all-electron wave functions in terms of the corresponding pseudo-wave-functions, overcoming difficulties associated to nonlocal operators. Using this correspondence, it has been possible to address within (ultrasoft) pseudopotential schemes a variety of observables, including hyperfine splittings,[10–13] dynamical charges,[14] magnetic susceptibilities,[15,16] and nuclear magnetic resonance shifts.[15,16]

Density-functional perturbational approaches have addressed a large variety of physical observables.[17] In particular, the perturbation due to an infinitesimal electric field could be treated and dielectric tensors obtained.[18,19] These approaches are mostly based on plane-wave basis sets and norm-conserving pseudopotentials. The extension to ultrasoft pseudopotentials has been achieved for the study of lattice dynamics.[20,21]

In a recent work, we successfully treated the linear response to an electric field within the ultrasoft pseudopotential framework, thereby making possible the calculation of the Raman spectra for a disordered model structure of vitreous silica.[22] In the present paper, we complement our previous work by providing a comprehensive account of the variational density-functional perturbational theory which we developed. Our perturbational approach only accounts for variations of valence wave functions and is derived from the all-electron formulation via the correspondence introduced in the projector augmented wave method. The perturbation due to the electric field is expressed in terms of a derivative with respect to the **k** vector in the Brillouin zone.[19] Dielectric tensors are then obtained via a two-step procedure. In the first step, the first-order derivative of the wave functions with respect to **k** is obtained by minimizing an auxiliary non-self-consistent functional. The result of this minimization is used to set up a variational functional expressing the second-order derivative of the energy with respect to the field. In the second step, this functional is minimized in a self-consistent way and the dielectric tensor is obtained. When applied to norm-conserving pseudopotentials, the present formulation is found to coincide with earlier ones[19] but gives insight in the underlying approximations. While we here focus on the ultrasoft pseudopotential scheme, the present formulation also applies to the projector augmented wave method. To validate our scheme, we calculate polarizability tensors and Raman intensities of small molecules, such as H_2O, CH_4, and NH_3, and find good agreement with both experimental data and previous all-electron results. Taking advantage of the ultrasoft pseudopotential scheme, our method is particularly suited to treat systems of relatively large size. In a previous application, we illustrated this potential by calculating the Raman spectra of model structures of vitreous silica.[22] We here complement this study by addressing the dielectric tensor of the same model structures.

The paper is organized as follows. In Sec. II, we outline how the correspondence between all-electron and pseudo-wave-functions, introduced in the projector augmented wave method, applies within the ultrasoft pseudopotential scheme. In Sec. III, we develop our perturbational theory for calculating dielectric tensors within the ultrasoft pseudopotential scheme. In Sec. IV, we calculate polarizabilities and Raman intensities for small molecules. We also calculate the static dielectric constants for disordered model structures of vitreous silica. The conclusions are drawn in Sec. V. In the Appendix, we describe the technical procedure adopted in this work for minimizing the variational functionals given in Sec. III.

II. RELATION BETWEEN ALL-ELECTRON AND PSEUDO-WAVE-FUNCTIONS

In the projector augmented wave method,[8] a linear operator T is introduced to connect an all electron wave function Ψ_n to its corresponding pseudo-wave-function $\tilde{\Psi}_n$:

$$|\Psi_n\rangle = T|\tilde{\Psi}_n\rangle. \tag{1}$$

This transformation allows one to treat valence states through soft pseudo-wave-functions, overcoming the difficulty of treating the strong oscillations of the all-electron wave functions in the core region. For simplicity, we consider here an electronic system describing the interaction with a single ionic core. The operator T reads[8]

$$T = 1 + \sum_i (|\Phi_i\rangle - |\tilde{\Phi}_i\rangle)\langle\beta_i|, \tag{2}$$

where Φ_i and $\tilde{\Phi}_i$ are all-electron and pseudo *atomic* wave functions, which coincide outside of the core region. This operator ensures that the pseudo-wave-function $\tilde{\Psi}_n$ matches the all-electron wave function Ψ_n outside of the core region. Inside the core region, the projectors β_i satisfy the following completeness relation:

$$\sum_i |\tilde{\Phi}_i\rangle\langle\beta_i| = 1. \tag{3}$$

Through the relation in Eq. (1), any operator A acting on all-electron wave functions corresponds to a pseudo-operator $\tilde{A}$ acting on pseudo-wave-functions:

$$\langle\Psi_n|A|\Psi_m\rangle = \langle\tilde{\Psi}_n|T^\dagger A T|\tilde{\Psi}_m\rangle = \langle\tilde{\Psi}_n|\tilde{A}|\tilde{\Psi}_m\rangle, \tag{4}$$

where $\tilde{A}$ is defined as $T^\dagger A T$. When the operator A is quasilocal (i.e., it depends locally on the wave functions and locally on the space derivatives of the wave functions), the respective pseudo operator $\tilde{A}$ is given by[8]

$$\tilde{A} = A + \sum_{i,j} |\beta_i\rangle(\langle\Phi_i|A|\Phi_j\rangle - \langle\tilde{\Phi}_i|A|\tilde{\Phi}_j\rangle)\langle\beta_j|, \tag{5}$$

which is obtained making explicit use of the completeness relation in Eq. (3). In practical implementations, only a finite set of projectors β_i is considered.[1,2,8]

We now apply this scheme to the all-electron Kohn-Sham Hamiltonian operator H^0:

$$H^0 = -\frac{\hbar^2}{2m}\nabla^2 + V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r}) + V_{\mathrm{loc}}(\mathbf{r}), \tag{6}$$

where $-\hbar^2\nabla^2/(2m)$ is the kinetic energy, V_{H} the Hartree potential, V_{xc} the exchange-correlation potential, and V_{loc} a local potential external to the electron system. The potentials V_{H} and V_{xc} depend self-consistently on the electron density. The pseudo-Hamiltonian $\tilde{H}^0 = T^\dagger H^0 T$ acting on the pseudo-wave-functions reads

$$\tilde{H}^0 = H^0 + \sum_{ij} |\beta_i\rangle D_{ij}\langle\beta_j|, \tag{7}$$

where, in the same notation of Ref. 1,

$$D_{ij} = D_{ij}^0 + \int_R Q_{ij}(\mathbf{r})[V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r}) + V_{\mathrm{loc}}(\mathbf{r})]d\mathbf{r}, \tag{8}$$

$$D_{ij}^0 = -\frac{\hbar^2}{2m}\int_R [\Phi_i^*(\mathbf{r})\nabla^2\Phi_j(\mathbf{r}) + \tilde{\Phi}_i^*(\mathbf{r})\nabla^2\tilde{\Phi}_j(\mathbf{r})]d\mathbf{r}. \tag{9}$$

In the latter equations, R denotes that the integral is limited to the core region of radius R and the augmentation functions Q_{ij} are defined as:

$$Q_{ij}(\mathbf{r}) = \Phi_i^*(\mathbf{r})\Phi_j(\mathbf{r}) - \tilde{\Phi}_i^*(\mathbf{r})\tilde{\Phi}_j(\mathbf{r}). \tag{10}$$

The pseudo-wave-functions satisfy the generalized orthonormality constraints

$$\langle\tilde{\Psi}_n|S|\tilde{\Psi}_m\rangle = \delta_{nm}, \tag{11}$$

where S is the pseudoidentity operator $T^\dagger T$. Similarly, a pseudodensity operator $K(\mathbf{r})$ is derived from the all-electron density operator $|\mathbf{r}\rangle\langle\mathbf{r}|$:

$$K(\mathbf{r}) = |\mathbf{r}\rangle\langle\mathbf{r}| + \sum_{i,j} |\beta_i\rangle Q_{ij}(\mathbf{r})\langle\beta_j|. \tag{12}$$

The pseudo-Kohn-Sham Hamiltonian obtained through relation (1), introduced in the projector augmented wave method, corresponds to that found in the ultrasoft pseudopotential scheme.[1] However, as opposed to the projector augmented wave method which is an all-electron scheme, the ultrasoft pseudopotential scheme treats explicitly only the valence wave functions. In pseudopotential approaches, there is a redefinition of the local part of the potential to account for the core electrons. The screening of the nuclei due to the core electrons, which contributes to the Hartree potential V_{H} in an all-electron Hamiltonian, is transferred to the local potential V_{loc} of the pseudo Hamiltonian.

The scheme outlined above can also be related to the norm-conserving pseudopotential scheme.[23] In the latter scheme, the following norm-conserving condition is imposed:

$$\int_R \Phi_i^*(\mathbf{r})\Phi_j(\mathbf{r})d\mathbf{r}=\int_R \tilde{\Phi}_i^*(\mathbf{r})\tilde{\Phi}_j(\mathbf{r})d\mathbf{r}, \tag{13}$$

which ensures that the total pseudocharge in the core region equals the corresponding all-electron charge, as can be deduced from Eqs. (12) and (10). Hence, the operator $S=T^\dagger T$ becomes the identity operator. Upon transformation (5), the kinetic energy operator gives rise to the nonlocal potential V_{NL} appearing in the pseudo-Hamiltonian (7):

$$V_{\mathrm{NL}}=\sum_{ij}|\beta_i\rangle D_{ij}^0\langle\beta_j|. \tag{14}$$

The norm-conserving pseudopotential scheme also adopts an additional approximation, which is generally not specified. In fact, one assumes not only that the integral of $Q_{ij}(\mathbf{r})$ vanishes as imposed by Eq. (13), but also that $Q_{ij}(\mathbf{r})$ vanishes everywhere:

$$Q_{ij}(\mathbf{r})=0. \tag{15}$$

The pseudodensity operator $K(\mathbf{r})$ then coincides with the all-electron one. In this way, the pseudo-Hamiltonian formally differs from the all-electron one only by the nonlocal potential V_{NL}.

We now extend the above formalism to the case of an infinite periodic system. According to the Bloch theorem, the all-electron wave functions can be written as

$$\Psi_{\mathbf{k}n}(\mathbf{r})=(2\pi)^{3/2}(\Omega)^{-1/2}e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}n}(\mathbf{r}), \tag{16}$$

where Ω is the volume of the primitive cell, $\mathbf{k}$ is a wave vector belonging to the Brillouin zone, and $u_{\mathbf{k}n}$ are periodic all-electron wave functions. The valence charge density is periodic and is expressed by (in units of electrons per cell):

$$n(\mathbf{r})=\frac{\Omega}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_v u_{\mathbf{k}v}^*(\mathbf{r})u_{\mathbf{k}v}(\mathbf{r})d\mathbf{k}, \tag{17}$$

where the integral is taken over the Brillouin zone, and the index v runs over the occupied valence states. For any operator A acting on the all-electron wave functions $\Psi_{\mathbf{k}n}$, we can define a corresponding operator $A_{\mathbf{k},\mathbf{k}'}$ acting on the Hilbert space of periodic functions $u_{\mathbf{k}n}(\mathbf{r})$:

$$A_{\mathbf{k},\mathbf{k}'}(\mathbf{r},\mathbf{r}')=e^{-i\mathbf{k}\cdot\mathbf{r}}A(\mathbf{r},\mathbf{r}')e^{i\mathbf{k}'\cdot\mathbf{r}'}. \tag{18}$$

In particular, the Kohn-Sham Hamiltonian operator is periodic and therefore diagonal when expressed on Bloch states.

For a periodic system, the operator T reads

$$T=1+\sum_{\mathbf{R},I,i}(|\Phi_{i,\mathbf{R},I}\rangle-|\tilde{\Phi}_{i,\mathbf{R},I}\rangle)\langle\beta_{i,\mathbf{R},I}|, \tag{19}$$

where the vector $\mathbf{R}$ describes the Bravais lattice and the index I runs over the ionic cores in the cell. The functions $\Phi_{\mathbf{R},I,i}$ and $\tilde{\Phi}_{\mathbf{R},I,i}$ are centered on the ionic cores and show the following translational property:

$$\begin{aligned}\Phi_{i,\mathbf{R},I}[\mathbf{r}-(\mathbf{R}+\tau_I)]&=\Phi_{i,I}(\mathbf{r}),\\ \tilde{\Phi}_{i,\mathbf{R},I}[\mathbf{r}-(\mathbf{R}+\boldsymbol{\tau}_I)]&=\tilde{\Phi}_{i,I}(\mathbf{r}),\\ \beta_{i,\mathbf{R},I}[\mathbf{r}-(\mathbf{R}+\boldsymbol{\tau}_I)]&=\beta_{i,I}(\mathbf{r}),\end{aligned} \tag{20}$$

where $\mathbf{R}+\tau_I$ is the position of the ion I in the cell labeled by the vector $\mathbf{R}$. The operator T has the periodicity of the lattice, and becomes diagonal when expressed on a basis set of periodic functions $u_{\mathbf{k}n}(\mathbf{r})$ as in Eq. (18). Hence, periodic pseudo-wave-functions $\tilde{u}_{\mathbf{k}n}$ are defined in a straightforward way:

$$|u_{\mathbf{k}n}\rangle=T_{\mathbf{k},\mathbf{k}}|\tilde{u}_{\mathbf{k}n}\rangle, \tag{21}$$

and can be used to express the pseudo-wave-function $\tilde{\Psi}_{\mathbf{k}n}$:

$$\tilde{\Psi}_{\mathbf{k}n}(\mathbf{r})=(2\pi)^{3/2}(\Omega)^{-1/2}e^{i\mathbf{k}\cdot\mathbf{r}}\tilde{u}_{\mathbf{k}n}(\mathbf{r}). \tag{22}$$

To simplify the notation, we indicate in the following with $A_{\mathbf{k}}$ the diagonal term $A_{\mathbf{k},\mathbf{k}}$ of a generic operator A.

We now generalize Eq. (5) to the case of operators acting on periodic wave functions. We define the following functions:

$$\begin{aligned}|\Phi_{i,\mathbf{R},I,\mathbf{k}}\rangle&=e^{-i\mathbf{k}(\mathbf{r}-\mathbf{R})}|\Phi_{i,\mathbf{R},I}\rangle,\\ |\tilde{\Phi}_{i,\mathbf{R},I,\mathbf{k}}\rangle&=e^{-i\mathbf{k}(\mathbf{r}-\mathbf{R})}|\tilde{\Phi}_{i,\mathbf{R},I}\rangle,\\ |\beta_{i,\mathbf{R},I,\mathbf{k}}\rangle&=e^{-i\mathbf{k}(\mathbf{r}-\mathbf{R})}|\beta_{i,\mathbf{R},I}\rangle.\end{aligned} \tag{23}$$

The operator $T_{\mathbf{k}}$ can then be expressed as:

$$T_{\mathbf{k}}=1+\sum_{i,\mathbf{R},I}(|\Phi_{i,\mathbf{R},I,\mathbf{k}}\rangle-|\tilde{\Phi}_{i,\mathbf{R},I,\mathbf{k}}\rangle)\langle\beta_{i,\mathbf{R},I,\mathbf{k}}|. \tag{24}$$

Using the completeness relation (3), we obtain for every vector $\mathbf{k}$:

$$\sum_i|\tilde{\Phi}_{i,\mathbf{R},I,\mathbf{k}}\rangle\langle\beta_{i,\mathbf{R},I,\mathbf{k}}|=1. \tag{25}$$

This relation can then be used to obtain an expression of the pseudo-operator $\tilde{A}_{\mathbf{k}}=T_{\mathbf{k}}^\dagger A_{\mathbf{k}}T_{\mathbf{k}}$, corresponding to the quasilocal operator A, in an analogous way as for Eq. (5):

$$\tilde{A}_{\mathbf{k}}=A_{\mathbf{k}}+\sum_{i,j,\mathbf{R},I}(|\beta_{i,\mathbf{R},I,\mathbf{k}}\rangle(\langle\Phi_{i,\mathbf{R},I,\mathbf{k}}|A_{\mathbf{k}}|\Phi_{j,\mathbf{R},I,\mathbf{k}}\rangle - \langle\tilde{\Phi}_{i,\mathbf{R},I,\mathbf{k}}|A_{\mathbf{k}}|\tilde{\Phi}_{j,\mathbf{R},I,\mathbf{k}}\rangle)\langle\beta_{j,\mathbf{R},I,\mathbf{k}}|). \tag{26}$$

III. VARIATIONAL FUNCTIONAL FOR $\boldsymbol{\epsilon}_\infty$ IN THE ULTRASOFT PSEUDOPOTENTIAL SCHEME

In this section, we develop a perturbational density-functional theory for obtaining dielectric tensors within the ultrasoft pseudopotential scheme, which also applies to the projector augmented wave method. Our formulation starts from the variational functional expressing the dielectric tensor as the second-order derivative of the energy with respect to the electric field purturbation within an all-electron formalism.[19] Then, using the correspondence between all-electron and pseudo-wave-functions outlined in the previous section,[8] we transform the all-electron functional to a pseudo one.

The dielectric tensor $\boldsymbol{\epsilon}_\infty$ is determined by the second order derivative of the energy with respect to the electric field:[19]

$$\epsilon_{\infty_{\alpha\beta}}=\delta_{\alpha\beta}-\frac{4\pi}{\Omega}\frac{\partial^2 E_{\mathrm{tot}}}{\partial\mathcal{E}_\alpha\partial\mathcal{E}_\beta}, \tag{27}$$

where the indices α and β correspond to the Cartesian directions of the electric field $\mathcal{E}$.

Adopting an all-electron scheme, the diagonal terms of the dielectric tensor can be obtained by minimizing the following selfconsistent variational functional with respect to the first order all-electron periodic wave functions $\partial u^0_{\mathbf{k}v}/\partial\mathcal{E}_\alpha$:[19]

$$\begin{aligned}\frac{1}{2}\frac{\partial^2 E_{\mathrm{tot}}}{\partial\mathcal{E}^2_\alpha}=&\frac{\Omega}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_v\left(\left\langle\frac{\partial}{\partial\mathcal{E}_\alpha}u^0_{\mathbf{k}v}\right|H^0_{\mathbf{k}}-\epsilon^0_{\mathbf{k}v}\left|\frac{\partial}{\partial\mathcal{E}_\alpha}u^0_{\mathbf{k}v}\right\rangle\right.\\&+\left\langle\frac{\partial}{\partial\mathcal{E}_\alpha}u^0_{\mathbf{k}v}\right|i\frac{\partial}{\partial k_\alpha}u^0_{\mathbf{k}v}\right\rangle\\&\left.+\left\langle i\frac{\partial}{\partial k_\alpha}u^0_{\mathbf{k}v}\right|\frac{\partial}{\partial\mathcal{E}_\alpha}u^0_{\mathbf{k}v}\right\rangle\right)d\mathbf{k}\\&+\frac{1}{2}\int\frac{n^1(\mathbf{r})n^1(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\\&+\frac{1}{2}\int\left.\frac{\delta V_{\mathrm{xc}}}{\delta n}\right|_{n^0}[n^1(\mathbf{r})]^2d\mathbf{r},\end{aligned} \tag{28}$$

where the index v runs over the occupied valence states, $u^0_{\mathbf{k}v}$ are the unperturbed periodic ground state wave functions of energy $\epsilon^0_{\mathbf{k}v}$, V_{xc} is the exchange-correlation potential, which, for simplicity, is taken as in the local-density approximation, n^0 is the unperturbed charge density, and n^1 is the first-order derivative of the charge density defined as

$$\begin{aligned}n^1(\mathbf{r})=&\frac{\Omega}{(2\pi)^3}\int_{\mathrm{BZ}}\left(\sum_v u^{0*}_{\mathbf{k}v}(\mathbf{r})\frac{\partial}{\partial\mathcal{E}_\alpha}u^0_{\mathbf{k}v}(\mathbf{r})\right.\\&\left.+\frac{\partial}{\partial\mathcal{E}_\alpha}u^{0*}_{\mathbf{k}v}(\mathbf{r})u^0_{\mathbf{k}v}(\mathbf{r})\right)d\mathbf{k}.\end{aligned} \tag{29}$$

For simplicity, we do not consider spin degeneracy and the electronic charge is taken unitary. The first-order wave functions $\partial u^0_{\mathbf{k}v}/\partial\mathcal{E}_\alpha$ satisfy the constraints:[19]

$$\left\langle\frac{\partial}{\partial\mathcal{E}_\alpha}u^0_{\mathbf{k}v}\middle|u^0_{\mathbf{k}v'}\right\rangle+\left\langle u^0_{\mathbf{k}v}\middle|\frac{\partial}{\partial\mathcal{E}_\alpha}u^0_{\mathbf{k}v'}\right\rangle=0, \tag{30}$$

where v and v' run over the occupied valence states. At the minimum, the first-order all-electron periodic wave functions $\partial u^0_{\mathbf{k}v}/\partial\mathcal{E}_\alpha$ fulfill the generalized Sternheimer equation (Euler-Lagrange equations associated to the minimization of the functional):[18]

$$\begin{aligned}(H^0_{\mathbf{k}}-\epsilon^0_{\mathbf{k}v})P_c(\mathbf{k})&\left|\frac{\partial}{\partial\mathcal{E}_\alpha}u^0_{\mathbf{k}v}\right\rangle\\&=-P_c(\mathbf{k})\left(i\frac{\partial}{\partial k_\alpha}+V^1_{\mathrm{H}}+V^1_{\mathrm{xc}}\right)|u^0_{\mathbf{k}v}\rangle,\end{aligned} \tag{31}$$

where $P_c(\mathbf{k})$ is the projector on the unoccupied subspace and results from the application of the constraints (30), and where the first-order variations of the Hartree and the exchange-correlation potentials read:

$$V^1_{\mathrm{H}}(\mathbf{r})=\int\frac{n^1(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \tag{32}$$

and

$$V^1_{\mathrm{xc}}(\mathbf{r})=\left.\frac{\delta V_{\mathrm{xc}}}{\delta n}\right|_{n^0}(\mathbf{r})n^1(\mathbf{r}). \tag{33}$$

The derivatives $\partial u^0_{\mathbf{k}v}/\partial k_\alpha$ appearing in Eqs. (28) and (31) can be calculated by minimizing a non-self-consistent variational functional.[19] The off-diagonal elements of the dielectric tensor can then be obtained from:[19]

$$\begin{aligned}\frac{\partial^2 E_{\mathrm{tot}}}{\partial\mathcal{E}_\alpha\partial\mathcal{E}_\beta}=&\frac{\Omega}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_v\left(\left\langle\frac{\partial}{\partial\mathcal{E}_\alpha}u^0_{\mathbf{k}v}\middle|i\frac{\partial}{\partial k_\beta}u^0_{\mathbf{k}v}\right\rangle\right.\\&\left.+\left\langle i\frac{\partial}{\partial k_\alpha}u^0_{\mathbf{k}v}\middle|\frac{\partial}{\partial\mathcal{E}_\beta}u^0_{\mathbf{k}v}\right\rangle\right)d\mathbf{k}.\end{aligned} \tag{34}$$

With the formalism developed in Sec. II, we can express the scheme for the calculation of dielectric tensors in terms of pseudo-wave-functions. The variational selfconsistent functional (28) then reads

$$\frac{1}{2}\frac{\partial^2 E_{\rm tot}}{\partial \mathcal{E}_\alpha^2}=\frac{\Omega}{(2\pi)^3}\int_{\rm BZ}\sum_v \left(\left\langle \frac{\partial}{\partial\mathcal{E}_\alpha}\tilde{u}^0_{\mathbf{k}v}\right| T^\dagger_{\mathbf{k}}(H^0_{\mathbf{k}}-\epsilon^0_{\mathbf{k}v})T_{\mathbf{k}}\left|\frac{\partial}{\partial\mathcal{E}_\alpha}\tilde{u}^0_{\mathbf{k}v}\right\rangle + \left\langle \frac{\partial}{\partial\mathcal{E}_\alpha}\tilde{u}^0_{\mathbf{k}v}\right|T^\dagger_{\mathbf{k}} i\frac{\partial}{\partial k_\alpha}T_{\mathbf{k}}\left|\tilde{u}^0_{\mathbf{k}v}\right\rangle + \left\langle\tilde{u}^0_{\mathbf{k}v}\right|T^\dagger_{\mathbf{k}}\left(i\frac{\partial}{\partial k_\alpha}\right)^\dagger T_{\mathbf{k}}\left|\frac{\partial}{\partial\mathcal{E}_\alpha}\tilde{u}^0_{\mathbf{k}v}\right\rangle\right)d\mathbf{k}+\frac{1}{2}\int\frac{n^1(\mathbf{r})n^1(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+\frac{1}{2}\int\left.\frac{\delta V_{\rm xc}}{\delta n}\right|_{n^0}[n^1(\mathbf{r})]^2 d\mathbf{r}, \tag{35}$$

where we explicitly used that the operator $T_{\mathbf{k}}$ does not depend on the electric field. This functional is minimized with respect to the first-order pseudo-wave-functions $\partial\tilde{u}^0_{\mathbf{k}v}/\partial\mathcal{E}_\alpha$ satisfying the constraints:

$$\left\langle\frac{\partial}{\partial\mathcal{E}_\alpha}\tilde{u}^0_{\mathbf{k}v}\right|T^\dagger_{\mathbf{k}}T_{\mathbf{k}}|\tilde{u}^0_{\mathbf{k}v'}\rangle+\left\langle\tilde{u}^0_{\mathbf{k}v}\right|T^\dagger_{\mathbf{k}}T_{\mathbf{k}}\left|\frac{\partial}{\partial\mathcal{E}_\alpha}\tilde{u}^0_{\mathbf{k}v'}\right\rangle=0. \tag{36}$$

We write this functional in a more compact form by introducing pseudo-operators

$$\frac{1}{2}\frac{\partial^2 E_{\rm tot}}{\partial \mathcal{E}_\alpha^2}=\frac{\Omega}{(2\pi)^3}\int_{\rm BZ}\sum_v \left(\left\langle \frac{\partial}{\partial\mathcal{E}_\alpha}\tilde{u}^0_{\mathbf{k}v}\right| \tilde{H}^0_{\mathbf{k}}-\epsilon_{\mathbf{k}v}S_{\mathbf{k}}\left|\frac{\partial}{\partial\mathcal{E}_\alpha}\tilde{u}^0_{\mathbf{k}v}\right\rangle + \left\langle \frac{\partial}{\partial\mathcal{E}_\alpha}\tilde{u}^0_{\mathbf{k}v}\right|T^\dagger_{\mathbf{k}} i\frac{\partial}{\partial k_\alpha}T_{\mathbf{k}}\left|\tilde{u}^0_{\mathbf{k}v}\right\rangle + \left\langle\tilde{u}^0_{\mathbf{k}v}\right|T^\dagger_{\mathbf{k}}\left(i\frac{\partial}{\partial k_\alpha}\right)^\dagger T_{\mathbf{k}}\left|\frac{\partial}{\partial\mathcal{E}_\alpha}\tilde{u}^0_{\mathbf{k}v}\right\rangle\right)d\mathbf{k}+\frac{1}{2}\int\frac{n^1(\mathbf{r})n^1(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+\frac{1}{2}\int\left.\frac{\delta V_{\rm xc}}{\delta n}\right|_{n^0}[n^1(\mathbf{r})]^2 d\mathbf{r}. \tag{37}$$

Similarly, the constraints become:

$$\left\langle\frac{\partial}{\partial\mathcal{E}_\alpha}\tilde{u}^0_{\mathbf{k}v}\right|S_{\mathbf{k}}\left|\,\tilde{u}^0_{\mathbf{k}v'}\right\rangle+\left\langle\tilde{u}^0_{\mathbf{k}v}\right|S_{\mathbf{k}}\left|\frac{\partial}{\partial\mathcal{E}_\alpha}\tilde{u}^0_{\mathbf{k}v'}\right\rangle=0. \tag{38}$$

The Sternheimer equation is now expressed in terms of $\partial\tilde{u}^0_{\mathbf{k}v}/\partial\mathcal{E}_\alpha$:[20]

$$(\tilde{H}^0_{\mathbf{k}}-\epsilon_{\mathbf{k}v}S_{\mathbf{k}})P_c(\mathbf{k})\left|\frac{\partial}{\partial\mathcal{E}_\alpha}\tilde{u}^0_{\mathbf{k}v}\right\rangle =-P^\dagger_c(\mathbf{k})\left(T^\dagger_{\mathbf{k}}i\frac{\partial}{\partial k_\alpha}T_{\mathbf{k}}+V^1_{\rm H}+V^1_{\rm xc}\right)|\tilde{u}^0_{\mathbf{k}v}\rangle. \tag{39}$$

where $P_c(\mathbf{k})$ and $P^\dagger_c(\mathbf{k})$ are generalized projectors on the unoccupied subspace, defined as

$$P_c(\mathbf{k})=1-\sum_v|\tilde{u}^0_{\mathbf{k}v}\rangle\langle\tilde{u}^0_{\mathbf{k}v}|S_{\mathbf{k}}, \tag{40}$$

and

$$P^\dagger_c(\mathbf{k})=1-\sum_v S_{\mathbf{k}}|\tilde{u}^0_{\mathbf{k}v}\rangle\langle\tilde{u}^0_{\mathbf{k}v}|. \tag{41}$$

In both definitions, the indices v run over the occupied pseudostates.

We give an explicit form to the operator $T^\dagger_{\mathbf{k}}i\partial/\partial k_\alpha T_{\mathbf{k}}$ by using Eq. (26):

$$\begin{aligned}T^\dagger_{\mathbf{k}}i\frac{\partial}{\partial k_\alpha}T_{\mathbf{k}}=i\frac{\partial}{\partial k_\alpha}+\sum_{i,j,\mathbf{R},I}\Bigg[&|\beta_{i,\mathbf{R},I,\mathbf{k}}\rangle\\ &\times\left(\left\langle\Phi_{i,\mathbf{R},I,\mathbf{k}}\right|i\frac{\partial}{\partial k_\alpha}\left|\Phi_{j,\mathbf{R},I,\mathbf{k}}\right\rangle-\left\langle\tilde{\Phi}_{i,\mathbf{R},I,\mathbf{k}}\right|i\frac{\partial}{\partial k_\alpha}\left|\tilde{\Phi}_{j,\mathbf{R},I,\mathbf{k}}\right\rangle\right)\langle\beta_{j,\mathbf{R},I,\mathbf{k}}|\\ &-\left|\beta_{i,\mathbf{R},I,\mathbf{k}}\right\rangle(\langle\Phi_{i,\mathbf{R},I,\mathbf{k}}|\Phi_{j,\mathbf{R},I,\mathbf{k}}\rangle-\langle\tilde{\Phi}_{i,\mathbf{R},I,\mathbf{k}}|\tilde{\Phi}_{j,\mathbf{R},I,\mathbf{k}}\rangle)\left\langle i\frac{\partial}{\partial k_\alpha}\beta_{j,\mathbf{R},I,\mathbf{k}}\right|\\ &+|\beta_{i,\mathbf{R},I,\mathbf{k}}\rangle(\langle\Phi_{i,\mathbf{R},I,\mathbf{k}}|\Phi_{j,\mathbf{R},I,\mathbf{k}}\rangle-\langle\tilde{\Phi}_{i,\mathbf{R},I,\mathbf{k}}|\tilde{\Phi}_{j,\mathbf{R},I,\mathbf{k}}\rangle)\langle\beta_{j,\mathbf{R},I,\mathbf{k}}|i\frac{\partial}{\partial k_\alpha}.\end{aligned} \tag{42}$$

By using Eqs. (23), we finally find

$$T_{\mathbf{k}}^{\dagger} i \frac{\partial}{\partial k_\alpha} T_{\mathbf{k}} = i \frac{\partial}{\partial k_\alpha} + \sum_{i,j,\mathbf{R},I} \Bigg[|\beta_{i,\mathbf{R},I,\mathbf{k}}\rangle d_{ij,I,\alpha} \langle \beta_{j,\mathbf{R},I,\mathbf{k}}| - |\beta_{i,\mathbf{R},I,\mathbf{k}}\rangle Q_{ij,I} \langle \beta_{j,\mathbf{R},I,\mathbf{k}}| (r_\alpha - R_\alpha)| + |\beta_{i,\mathbf{R},I,\mathbf{k}}\rangle Q_{ij,I} \langle \beta_{j,\mathbf{R},I,\mathbf{k}}| i \frac{\partial}{\partial k_\alpha} \Bigg], \tag{43}$$

where

$$Q_{ij,I} = \langle \Phi_{i,\mathbf{R},I,\mathbf{k}} | \Phi_{j,\mathbf{R},I,\mathbf{k}} \rangle - \langle \tilde{\Phi}_{i,\mathbf{R},I,\mathbf{k}} | \tilde{\Phi}_{j,\mathbf{R},I,\mathbf{k}} \rangle \tag{44}$$

$$\mathbf{d}_{ij,I} = \langle \Phi_{i,\mathbf{R},I,\mathbf{k}} | \mathbf{r} - \mathbf{R} | \Phi_{j,\mathbf{R},I,\mathbf{k}} \rangle - \langle \tilde{\Phi}_{i,\mathbf{R},I,\mathbf{k}} | \mathbf{r} - \mathbf{R} | \tilde{\Phi}_{j,\mathbf{R},I,\mathbf{k}} \rangle. \tag{45}$$

The parameters $Q_{ij,I}$ and $\mathbf{d}_{ij,I}$ do not depend on the particular cell labeled by $\mathbf{R}$ and can easily be calculated.

We note that the operator given in Eq. (42) generalizes the Berry phase definition of the polarization P to the ultrasoft pseudopotential scheme.[24] Indeed, for a set of periodic wave functions $\{\tilde{u}_{\mathbf{k},v}\}$, the polarization reads:

$$P = \frac{\Omega}{(2\pi)^3} \int_{\mathrm{BZ}} \sum_v \left\langle \tilde{u}_{\mathbf{k}v} \middle| T_{\mathbf{k}}^{\dagger} i \frac{\partial}{\partial k_\alpha} T_{\mathbf{k}} \middle| \tilde{u}_{\mathbf{k}v} \right\rangle + \text{c.c.}, \tag{46}$$

which can be expressed explicitly through Eq. (43). The resulting expression is the same as that obtained previously through a procedure based on Wannier functions.[25]

The expression obtained in Eq. (43) for ultrasoft pseudopotentials extends the analogous one for norm-conserving pseudopotentials. In the norm-conserving pseudopotential scheme,[19] the summation on the right-hand side of Eq. (43) does not appear:

$$T_{\mathbf{k}}^{\dagger} i \frac{\partial}{\partial k_\alpha} T_{\mathbf{k}} = i \frac{\partial}{\partial k_\alpha}. \tag{47}$$

In fact, the parameters $Q_{ij,I}$ vanish for norm-conserving pseudopotentials, due to relation (13). The first term in the summation, on the right-hand side of Eq. (43), can be neglected only when the additional approximation (15) is assumed.

The exposed scheme requires the determination of the first-order derivative of the pseudo-wave-functions $\partial \tilde{u}_{\mathbf{k}v}^0 / \partial k_\alpha$ with respect to a variation of the $\mathbf{k}$ vector in the Brillouin zone. These derivatives can be determined by the application of a variational nonselfconsistent perturbational scheme.[19] For each $\mathbf{k}$ point, we minimize the second-order energy functional obtained by an expansion with respect to the $\mathbf{k}$ vector. Generalizing the expression obtained in Ref. 19 for norm-conserving pseudopotentials to ultrasoft ones, we obtain

$$\frac{1}{2} \frac{\partial^2 E_{\mathbf{k}v}}{\partial k_\alpha^2} = \left\langle \frac{\partial}{\partial k_\alpha} \tilde{u}_{\mathbf{k}v}^0 \middle| \tilde{H}_{\mathbf{k}}^0 - \epsilon_{\mathbf{k}}^0 S_{\mathbf{k}} \middle| \frac{\partial}{\partial k_\alpha} \tilde{u}_{\mathbf{k}v}^0 \right\rangle + \left\langle \frac{\partial}{\partial k_\alpha} \tilde{u}_{\mathbf{k}v}^0 \middle| \frac{\partial}{\partial k_\alpha} \tilde{H}_{\mathbf{k}}^0 - \epsilon_{\mathbf{k}}^0 \frac{\partial}{\partial k_\alpha} S_{\mathbf{k}} \middle| \tilde{u}_{\mathbf{k}v}^0 \right\rangle + \left\langle \tilde{u}_{\mathbf{k}v}^0 \middle| \frac{\partial}{\partial k_\alpha} \tilde{H}_{\mathbf{k}}^0 - \epsilon_{\mathbf{k}}^0 \frac{\partial}{\partial k_\alpha} S_{\mathbf{k}} \middle| \frac{\partial}{\partial k_\alpha} \tilde{u}_{\mathbf{k}v}^0 \right\rangle, \tag{48}$$

where constant terms have been omitted and the first-order wave functions satisfy the constraints:

$$\left\langle \frac{\partial}{\partial k_\alpha} \tilde{u}_{\mathbf{k}v}^0 \middle| S_{\mathbf{k}} \middle| \tilde{u}_{\mathbf{k}v'}^0 \right\rangle + \left\langle \tilde{u}_{\mathbf{k}v}^0 \middle| S_{\mathbf{k}} \middle| \frac{\partial}{\partial k_\alpha} \tilde{u}_{\mathbf{k}v'}^0 \right\rangle + \left\langle \tilde{u}_{\mathbf{k}v}^0 \middle| \frac{\partial}{\partial k_\alpha} S_{\mathbf{k}} \middle| \tilde{u}_{\mathbf{k}v'}^0 \right\rangle = 0. \tag{49}$$

At the minimum, the first-order wave functions fulfill the corresponding Sternheimer equation:[20]

$$(\tilde{H}_{\mathbf{k}}^0 - \epsilon_{\mathbf{k}}^0 S_{\mathbf{k}}) P_c(\mathbf{k}) \left| \frac{\partial}{\partial k_\alpha} \tilde{u}_{\mathbf{k}v}^0 \right\rangle = -P_c^{\dagger}(\mathbf{k}) \left(\frac{\partial}{\partial k_\alpha} \tilde{H}_{\mathbf{k}}^0 - \epsilon_{\mathbf{k}}^0 \frac{\partial}{\partial k_\alpha} S_{\mathbf{k}} \right) |\tilde{u}_{\mathbf{k}v}^0\rangle. \tag{50}$$

The operators $(\partial/\partial k_\alpha)\tilde{H}_{\mathbf{k}}^0$ and $(\partial/\partial k_\alpha)\tilde{S}_{\mathbf{k}}$ are calculated from

$$\frac{\partial}{\partial k_\alpha} \tilde{H}_{\mathbf{k}}^0 = i[\tilde{H}^0, r_\alpha]_{\mathbf{k}}, \tag{51}$$

$$\frac{\partial}{\partial k_\alpha} \tilde{S}_{\mathbf{k}} = i[\tilde{S}, r_\alpha]_{\mathbf{k}}. \tag{52}$$

These relations follow directly from the definition given in Eq. (18).

IV. APPLICATIONS

In the present section, we assess the validity of our scheme for obtaining dielectric tensors with ultrasoft pseudopotentials by studying small molecules for which accurate all-electron results are available. We also apply our scheme to a disordered model of vitreous silica with a relatively large simulation cell to illustrate the potential of our method. Since we are interested in treating systems of relative large size, we here sample the Brillouin zone at the sole Γ point. We refer to the Appendix for a technical description of the applied minimization schemes.

A. Small molecules

We consider three small molecules, namely, the water, the methane, and the ammonia molecule. For these molecules, we address both the polarizability tensors and the Raman intensities.

The polarizability tensors are defined as the second-order derivative of the electronic energy with respect to the electric field:

TABLE I. Polarizabilty tensor of the water, the methane and the ammonia molecules. The Cartesian axes are chosen to correspond with the principal axes of the polarizability tensor. The permanent dipole moment of H_2O and of NH_3 is aligned along the z direction. The H_2O molecule is placed on the xy plane. The polarizabilities are given in Å^3.

	α_{xx}	α_{yy}	α_{zz}
H_2O			
Present	1.60	1.62	1.65
Ref. 39	1.60	1.59	1.62
Ref. 40	1.57	1.50	1.55
Expt. (Ref. 41)	1.48	1.37	1.43
Expt. (Ref. 42)	1.52	1.42	1.47
CH_4			
Present	2.70	2.70	2.70
Ref. 39	2.68	2.68	2.68
Ref. 40	2.59	2.59	2.59
Expt. (Ref. 43)	2.59	2.59	2.59
NH_3			
Present	2.22	2.22	2.66
Ref. 40	2.14	2.14	2.28
Expt. (Ref. 44)	2.07	2.07	2.48

TABLE II. Raman intensities (I), frequencies (ω) and depolarization ratios (ρ) of the water molecule. The Raman intensities are given in Å^4 amu^{-1} and the frequencies in cm^{-1}. The results of Refs. 38 and 45 are obtained within all-electron schemes. The experimental values are taken from Ref. 42.

Theory							Expt.		
Present			Ref. 38		Ref. 45		Ref. 42		
ω	I	ρ	ω	I	I	ρ	ω	I	ρ
1502	0.71	0.61	1547	0.67	1.0	0.59	1595	0.9 ± 2	0.74
3725	119	0.05	3714	110	111	0.04	3657	108 ± 14	0.03
3848	25.6	0.75	3823	24.9	25	0.75	3756	19.2 ± 2.1	0.75

$$\alpha_{\mu\nu}=\frac{\partial^2 E_{\mathrm{tot}}}{\partial\mathcal{E}_\mu\partial\mathcal{E}_\nu}, \tag{53}$$

and are calculated with the scheme described in the previous sections.

To calculate the Raman intensities, two ingredients are required: the derivatives of the polarizability tensor with respect to the atomic displacements, and the vibrational frequencies and modes. We obtain the derivatives of $\alpha_{\mu\nu}$ with respect to the atomic positions by finite differences

$$P_{\mu\nu,I\gamma}=\frac{\partial\alpha_{\mu\nu}}{\partial R_{I\gamma}}, \tag{54}$$

where the index I runs over the atoms of the molecule and the index γ runs over the Cartesian directions. The vibrational modes and frequencies are obtained by diagonalizing the dynamical matrix given by

$$D_{I\alpha,J\beta}=\frac{1}{\sqrt{M_I M_J}}\frac{\partial^2 E_{\mathrm{tot}}}{\partial R_{I\alpha}\partial R_{J\beta}}, \tag{55}$$

where M_I and M_J are the masses of atoms I and J, respectively. We calculate the dynamical matrix by taking finite differences of the atomic forces.

The Raman tensors are defined as the derivative of the polarizability with respect to the vibrational modes and can be expressed as

$$R^n_{\mu\nu}=\sum_{I\gamma} P_{\mu\nu,I\gamma}\frac{v^n_{I\gamma}}{\sqrt{M_I}}, \tag{56}$$

where v^n is the normalized nth eigenmode. When no particular choice is made for the polarization of the observed outgoing photons, the Raman intensity I^n of the nth mode results from an average over spatial orientations:[26]

$$I^n=d^n(45a_n^2+7c_n^2), \tag{57}$$

where d^n is the degeneracy of the nth mode and

$$a_n=\tfrac{1}{3}(R^n_{11}+R^n_{22}+R^n_{33}) \tag{58}$$

$$c_n^2=\tfrac{1}{2}\{(R^n_{11}-R^n_{22})^2+(R^n_{11}-R^n_{33})^2+(R^n_{22}-R^n_{33})^2 + 6[(R^n_{12})^2+(R^n_{13})^2+(R^n_{23})^2]\}. \tag{59}$$

For every mode n, the depolarization ratio ρ^n gives the ratio between the intensities observed when the polarizations of the incoming and outgoing photons are perpendicular and parallel:

$$\rho^n=\frac{3c_n^2}{45a_n^2+4c_n^2}. \tag{60}$$

The depolarization ratio can vary from zero to 3/4, and vanishes for totally symmetric modes.

We describe the electronic structure of the three molecules using ultrasoft pseudopotentials for all the involved atoms. The valence wave functions and the electron density are described by plane-wave basis sets defined by cutoff energies of 40 and 160 Ry, respectively. We checked that our results are fully converged with this choice of cutoff energies. The exchange and correlation energy is given within the local density approximation. We use a cubic simulation cell with a side of 25 bohrs, sufficiently large for yielding results for isolated molecules.[27] The displacements used in the finite-difference calculation of the Raman tensors and the dynamical matrices are taken to be of ±0.05 bohr. For these displacements, the polarizabilities and the forces are in the linear regime.

The structure of the investigated molecules was obtained by full relaxation within our theoretical scheme.[1] For the water molecule, we find a O-H bond length of 1.85 bohrs and a H-O-H angle of 105.9°, close to the corresponding experimental values (1.81 bohr and 104.5°).[28] The methane molecule is found to have a C-H bond length of 2.10 bohrs, in good agreement with the experimental bond length of 2.05

TABLE III. Raman intensities (I), frequencies (ω) and depolarization ratios (ρ) of the methane molecule. The Raman intensities are given in Å^4 amu^{-1} and the frequencies in cm^{-1}. The results of Refs. 38 and 45 are obtained within all-electron schemes. The experimental values are taken from Ref. 46.

Theory							Expt.		
Present			Ref. 38		Ref. 45		Ref. 46		
ω	I	ρ	ω	I	I	ρ	ω	I	ρ
1226	0.11	0.75	1250	0.27	0.01	0.75	1306	$\leqslant 0.24$	0.75
1469	2.6	0.75	1480	4.40	7.4	0.75	1534	7.0 ± 0.4	0.75
2940	254	0	2957	247	252	0	2917	230 ± 12	0
3053	144	0.75	3085	141	149	0.75	3019	128 ± 7	0.75

bohrs.[28] The relaxation of the atomic positions of the NH_3 molecule yields a N-H bond length of 1.95 bohrs and a H-N-H angle of 105.5°, to be compared with the experimental values of 1.91 bohrs and 106.7°.[28]

In Table I, we report calculated values for the polarizabilities of the H_2O, CH_4, and NH_3 molecules. For comparison, the table also contains experimental data and all-electron results obtained with localized basis sets. The all-electron results were obtained within the same local-density approximation for the exchange-correlation energy as used in the present work. Compared to the all-electron results, our data differ by at most 7%. This difference cannot simply be attributed to the frozen core approximation. In fact, various all-electron results in the literature show differences of the same order. Compared to the experimental data, our calculated polarizabilities are higher by at most 7%. We note that our calculated polarizabilities are allways higher than the experimental values. The theoretical overestimation due to the local density approximation is well known.[29]

Our results for the Raman intensities of the H_2O, CH_4, and NH_3 molecules are summarized in Tables II, III, and IV, respectively. Each table contains the vibrational frequencies and the corresponding Raman intensities and depolarization ratios for its respective molecule. We also report in the tables experimental data and all-electron results obtained with localized basis sets. The all-electron results were obtained within the same local-density approximation for the exchange-correlation energy as used in the present work.

TABLE IV. Raman intensities (I), frequencies (ω) and depolarization ratios (ρ) of the ammonia molecule. The Raman intensities are given in Å^4 amu^{-1} and the frequencies in cm^{-1}. The results of Ref. 45 are obtained within an all-electron scheme. The experimental values are taken from Ref. 47.

Theory					Expt.	
Present			Ref. 45		Ref. 47	
ω	I	ρ	I	ρ	ω	I
959	3.4	0.26	1.4	0.23	950	
1571	1.48	0.75	4.5	0.75	1627	
3395	191.4	0.01	208	0.01	3337	182 ± 2
3504	80.7	0.75	104	0.75	3444	

The vibrational frequencies calculated in the ultrasoft pseudopotential and all-electron schemes differ by at most 3%. Differences in Raman intensities amount to at most 20 Å^4 amu^{-1}, corresponding to a relative error of about 10% when referred to the highest intensity. All the trends are well reproduced with larger relative errors for the weakest lines. We note that, for the weak modes at low frequencies, significant differences are also observed between the intensities obtained with different all-electron schemes. Overall, we therefore conclude that the agreement with all-electron schemes is highly satisfactory. The comparison with experimental data is of the same quality.

B. Vitreous silica

We apply our scheme for the dielectric tensor to a disordered model structure of vitreous silica consisting of 72 atoms at the experimental density ($2.20\ \text{g/cm}^3$).[30] We refer to Ref. 30 for a detailed description of the structural properties, such as bond lengths and angles, and to Ref. 31 for a description in terms of ring statistics. This model has proved very successful in a series of previous investigations concerning the vibrational properties. These include the neutron vibrational density of states,[32,33] the infrared absorption spectrum,[14] the dynamical structure factor,[33] and vibrational amplitudes.[34] In particular, we used this model structure to calculate Raman spectra in the same way as above for the small molecules.[22] The analysis of the Raman spectra allowed us to give an estimation for the concentration of small ring structures in vitreous silica.[22]

We describe the electronic structure within the local-density approximation to density functional theory. We use a norm-conserving pseudopotential for Si (Ref. 35) and an ultrasoft pseudopotential for O (Ref. 2). The electron wave functions and charge density are described by plane-wave basis sets with cutoff energies of 24 and 200 Ry, respectively. The Brillouin zone is sampled at the Γ point.

Using the scheme outlined in the previous sections, we obtain the following dielectric tensor for this model structure of vitreous silica:

$$\epsilon_\infty = \begin{pmatrix} 2.12 & 0.03 & 0.01 \\ 0.03 & 2.14 & 0.00 \\ 0.01 & 0.00 & 2.15 \end{pmatrix}.$$

For an isotropic material, the dielectric tensor is proportional to the identity tensor. Because of the finite size of our model structure, the calculated tensor shows deviations with respect to the isotropic case. However, these deviations are small, namely at most 0.03. This implies that the dielectric constant is well described by a model structure of this size. We obtain an average dielectric constant of 2.14, in good agreement with the experimental result of 2.20.[36]

Despite the good agreement between calculated and experimental dielectric constants, the theoretical underestimation appears surprising in view of the tendency of the local-density approximation for overestimation.[29] To examine whether the underestimation relates with the presence of a high concentration of small rings in our model structure,[31] we also consider a second model of the same size but with a concentration of small rings in closer agreement with experiment.[22] Applying our scheme to the second model, we obtain the following dielectric tensor:

$$\epsilon_\infty = \begin{pmatrix} 2.19 & 0.03 & 0.02 \\ 0.03 & 2.30 & 0.01 \\ 0.02 & 0.01 & 2.28 \end{pmatrix}.$$

The corresponding average dielectric constant of 2.26 now overestimates the experimental value (2.20), in accord with the tendency of the local density approximation. Hence, the calculated values of the dielectric constants further favor the structure of the second model with respect to that of the first one.[22]

V. CONCLUSIONS

We introduced a variational density-functional perturbational scheme for calculating dielectric tensors within an ultrasoft pseudopotential framework. Our work makes use of a relation between all-electron and pseudo-wave-functions, first proposed in the projector augmented wave method.[8] This relation allows us to derive the coupling of the electric field to the pseudo-Hamiltonian from that in the all-electron one. Our scheme covers the cases of both ultrasoft and norm-conserving pseudopotentials. In the latter case, our scheme is found to coincide with previous treatments[19] but provides additionally a better understanding of the underlying approximations. Furthermore, our scheme overcomes the difficulty associated to the coupling of electric fields to nonlocal potentials in pseudo-Hamiltonians.[37] In fact, the coupling to the electric field is defined in our work at the level of the all-electron Hamiltonian which is intrinsically local, and is only subsequently transferred to the pseudo-Hamiltonian via the correspondence between all-electron and pseudo-wave-functions. In addition, our formulation applies by construction to the all-electron projector augmented wave method.[8]

We assessed the validity of our scheme by comparing calculated polarizabilities and Raman intensities for small molecules to corresponding data obtained with all-electron schemes. Our results are close to both all-electron and experimental data, supporting the validity of our perturbational scheme. The satisfactory agreement between experimental Raman intensities and those calculated within our scheme supports the notion that pseudopotential calculations of Raman intensities generally perform well, at variance with results of previous studies.[38]

The use of ultrasoft pseudopotentials in our scheme provides a computationally effective tool for calculating dielectric tensors and Raman intensities for systems of relatively large size. Indeed, the methodology described in this work was already successfully applied to the study of Raman intensities of vitreous silica.[22]

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APPENDIX: MINIMIZATION SCHEMES

We implemented the present formulation for the calculation of dielectric tensors within the ultrasoft pseudopotential scheme developed in Ref. 1. Since we are interested in treating systems of relative large size, we here sample the Brillouin zone at the sole Γ point. The unperturbed wave functions can therefore be taken real.

The first step requires the determination of the derivatives of the unperturbed wave functions with respect to the **k** vector through the minimization of the non-self-consistent functional (48). When a Γ-point sampling is adopted, the first-order wave functions can be taken purely imaginary. In the present implementation, we minimize functional (48) by performing a damped Car-Parrinello molecular dynamics[48] for the degrees of freedom that specify the first-order wave functions.

We explored two different schemes for imposing the constraints (49) when minimizing functional (48). The first scheme consists in using Lagrange multipliers $\lambda_{vv'}(\mathbf{k})$. This results in the addition of the constraints to the second-order energy functional (48):

$$\begin{aligned} \frac{1}{2}\frac{\partial^2 E'_{\mathbf{k}v}}{\partial k_\alpha^2} = {} & \left\langle \frac{\partial}{\partial k_\alpha}\tilde{u}^0_{\mathbf{k}v} \middle| \tilde{H}^0_{\mathbf{k}} - \epsilon^0_{\mathbf{k}} S_{\mathbf{k}} \middle| \frac{\partial}{\partial k_\alpha}\tilde{u}^0_{\mathbf{k}v} \right\rangle \\ & + \left\langle \frac{\partial}{\partial k_\alpha}\tilde{u}^0_{\mathbf{k}v} \middle| \frac{\partial}{\partial k_\alpha}\tilde{H}^0_{\mathbf{k}} - \epsilon^0_{\mathbf{k}} \frac{\partial}{\partial k_\alpha} S_{\mathbf{k}} \middle| \tilde{u}^0_{\mathbf{k}v} \right\rangle \\ & + \left\langle \tilde{u}^0_{\mathbf{k}v} \middle| \frac{\partial}{\partial k_\alpha}\tilde{H}^0_{\mathbf{k}} - \epsilon^0_{\mathbf{k}} \frac{\partial}{\partial k_\alpha} S_{\mathbf{k}} \middle| \frac{\partial}{\partial k_\alpha}\tilde{u}^0_{\mathbf{k}v} \right\rangle \\ & - \sum_{v'} \lambda_{vv'}(\mathbf{k}) \left(\left\langle \frac{\partial}{\partial k_\alpha}\tilde{u}^0_{\mathbf{k}v} \middle| S_{\mathbf{k}} | \tilde{u}^0_{\mathbf{k}v'} \right\rangle \right. \\ & \left. + \left\langle \tilde{u}^0_{\mathbf{k}v} | S_{\mathbf{k}} \middle| \frac{\partial}{\partial k_\alpha}\tilde{u}^0_{\mathbf{k}v'} \right\rangle + \left\langle \tilde{u}^0_{\mathbf{k}v} | \frac{\partial}{\partial k_\alpha} S_{\mathbf{k}} | \tilde{u}^0_{\mathbf{k}v'} \right\rangle \right), \quad \text{(A1)} \end{aligned}$$

where the **k** vector indicates the Γ point in our implementation. During the minimization, we obtain the Lagrange multipliers by imposing the constraints (49) at each Car-Parrinello step. This results in a procedure analogous to that described in Ref. 1 for the Car-Parrinello evolution of unperturbed wave functions.

In the second scheme, the constraints (49) are imposed by projecting the first-order wave functions on the unoccupied subspace. At the minimum of functional (A1), the following explicit expression for the Lagrange multipliers holds:

$$\lambda_{vv'}(\mathbf{k}) = \left\langle \tilde{u}^0_{\mathbf{k}v} \middle| \tilde{H}^0_{\mathbf{k}} - \epsilon^0_{\mathbf{k}v} S_{\mathbf{k}} \middle| \frac{\partial}{\partial k_\alpha} \tilde{u}^0_{\mathbf{k}v'} \right\rangle + \left\langle \tilde{u}^0_{\mathbf{k}v} \middle| \frac{\partial}{\partial k_\alpha} \tilde{H}^0_{\mathbf{k}} - \epsilon^0_{\mathbf{k}v} \frac{\partial}{\partial k_\alpha} S_{\mathbf{k}} \middle| \frac{\partial}{\partial k_\alpha} \tilde{u}^0_{\mathbf{k}v'} \right\rangle . \quad \text{(A2)}$$

Substituting this expression into the functional (A1), we obtain the following condition at its minimum:

$$\frac{\delta}{\delta \left\langle \frac{\partial}{\partial k_\alpha} \tilde{u}^0_{\mathbf{k}v} \right|} \left(\frac{\partial^2 E'_{\mathbf{k}v}}{\partial k_\alpha^2} \right) = P_c^\dagger(\mathbf{k}) \frac{\delta}{\delta \left\langle \frac{\partial}{\partial k_\alpha} \tilde{u}^0_{\mathbf{k}v} \right|} \left(\frac{\partial^2 E_{\mathbf{k}v}}{\partial k_\alpha^2} \right) = 0, \quad \text{(A3)}$$

where the functional derivative of the second-order expression (A1) is related, through some algebra, to that of functional (48).

Inspired by the conditions at the minimum, we proceed as follows in the second minimization scheme. We start from a trial set of first-order wave functions satisfying the constraints (49). The functional (48) subject to the constraints (49) is minimized by evolving the wave functions according to the gradient:

$$P_c^\dagger(\mathbf{k}) \frac{\delta}{\delta \left\langle \frac{\partial}{\partial k_\alpha} \tilde{u}^0_{\mathbf{k}v} \right|} \left(\frac{\partial^2 E_{\mathbf{k}v}}{\partial k_\alpha^2} \right). \quad \text{(A4)}$$

At each Car-Parrinello step, we then project the evolved wave functions on the unoccupied subspace by applying the operator $P_c(\mathbf{k})$ to ensure that the constraints (49) are satisfied. We verified that the two minimization schemes proposed here yield equivalent first-order wave functions at the minimum.

The second step requires the minimization of the self-consistent variational functional (37) with the constraints (38). Due to the Γ-point sampling, the first-order derivative of the Bloch wave functions with respect to the electric field can be taken real. As for the functional (48), we perform the minimization of functional (37) using a damped Car-Parrinello dynamics. The constraints (38) do not depend on the perturbation and can be implemented using either of the two schemes proposed above. During the minimization of functional (37), the first-order variation of the electronic charge is calculated at each step and the selfconsistent potential is updated. Minimization of functional (37) gives direct access to the diagonal elements of the dielectric tensor (27). The off-diagonal elements of the dielectric tensor are obtained from Eq. (34), expressed in terms of pseudo-wave-functions:

$$\frac{\partial^2 E_{\text{tot}}}{\partial \mathcal{E}_\alpha \partial \mathcal{E}_\beta} = \frac{\Omega}{(2\pi)^3} \int_{\text{BZ}} \sum_v \left\langle \frac{\partial}{\partial \mathcal{E}_\alpha} \tilde{u}^0_{\mathbf{k}v} \middle| T^\dagger_{\mathbf{k}} i \frac{\partial}{\partial k_\beta} T_{\mathbf{k}} \middle| \tilde{u}^0_{\mathbf{k}v} \right\rangle d\mathbf{k} + \text{c.c.}, \quad \text{(A5)}$$

where c.c. stands for complex conjugate and the operator $T^\dagger_{\mathbf{k}} i(\partial/\partial k_\beta) T_{\mathbf{k}}$ given explicitly in Eq. (42) is used.

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