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Density-functional perturbation theory for lattice dynamics with ultrasoft pseudopotentials

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We generalize density-functional perturbation theory for lattice dynamics to Vanderbilt's ultrasoft pseudopotential scheme. This formulation accounts for the nonorthogonality of the orbitals, the augmentation of the electron density, and the dependence of the generalized orthogonality constraint on the atomic positions. Both insulating and metallic systems are considered. Application of the theory to the vibrations of small molecules (CO, CO_2, CH_4, and H_2O) and to the phonon dispersion of the noble metals (Cu, Ag, Au) shows overall agreement with experiment. [S0163-1829(97)51742-5]

Density-functional perturbation theory (DFPT) has successfully been applied to first-principles calculations of linear[1,2] and nonlinear response[3] properties of materials, leading to a deeper understanding of the interplay between electronic and dynamical properties. In particular, it has become possible to calculate phonons at arbitrary wavelength,[4] dielectric and piezoelectric tensors,[5] Born effective charges, electron-phonon interactions,[6] infrared and Raman spectra,[7] and several other experimentally measurable quantities.

In the early applications to solids,[1,2] DFPT was formulated for norm-conserving pseudopotentials (PP's) and plane wave (PW) basis sets. The theory turns out to be conceptually simple in this basis since the same set of PW's describes both the unperturbed and the perturbed system. The only drawback of PW's is the rapid increase of the basis size with the range of localization of the electronic orbitals. This puts limitations on the type of atoms which can be afforded in large size systems. The most critical cases are the first-row transition metals and the first-row elements containing $3d$ and $2p$ valence electrons, respectively. Also, atoms where semicore states need to be included among the valence electrons might be difficult to describe with PW's.

There are several electronic structure schemes which deal efficiently with localized electrons. Among these, all-electron methods provide a full description of the electronic states. DFPT has been successfully applied within these approaches[8,9] to several challenging systems, such as perovskite materials,[10] and high-temperature superconductors.[11] However, in order to address systems of larger size, it remains of interest to treat localized electrons within a PP scheme.

Recently, an approach based on PW basis sets and ultrasoft PP's has been introduced to deal with localized electrons.[12,13] In this scheme, the orbitals are allowed to be as soft as possible in the core regions so that their expansion in PW's converges rapidly, but are required to satisfy a generalized orthonormality constraint which depends on the ionic positions. The full electron density is recovered by adding to the square modulus of the orbitals an augmentation charge localized in the core regions. Despite these technical complications, this approach has proved to be extremely successful in treating large-scale electronic structure problems. Using first-principles molecular dynamics, several systems containing first-row elements and transition metals, such as liquid copper,[13] water,[14] or disordered SiO_2 structures,[15] have been investigated. Furthermore, applications to solids have shown that the valence-electron properties obtained with the ultrasoft PP approach agree closely with all-electron results.[16]

In this paper we generalize DFPT for lattice dynamics to the ultrasoft PP scheme. The theory accounts for the nonorthogonality of the orbitals, the augmentation of the electron density, and the dependence of the generalized orthogonality constraint on the atomic positions. In fact, in the case of lattice dynamics, the perturbation displaces the augmentation charges and modifies the orthogonality constraint. We demonstrate the effectiveness of our approach in treating localized $2p$ electrons by applying it to the study of the vibrations of several molecules. Furthermore, we use the present formulation, generalized to metallic systems, to obtain the phonon spectra of noble metals (Cu, Ag, Au).

In the ultrasoft scheme the total energy of an insulating system containing N electrons is $E_{tot}[\psi_i]=\overline{E[\psi_i]}+F[\rho(\mathbf{r})]+U_{II}$ where (in a.u.)

$$\overline{E[\psi_i]}=-\frac{1}{2}\sum_i \langle\psi_i|\nabla^2|\psi_i\rangle+\sum_i \langle\psi_i|V_{NL}|\psi_i\rangle,$$

$$F[\rho(\mathbf{r})]=\int d^3r \;\; V_{loc}(\mathbf{r})\rho(\mathbf{r})+E_{Hxc}[\rho(\mathbf{r})],$$

and U_{II} is the ion-ion interaction. In this expression V_{NL} is the nonlocal PP, V_{loc} the local PP, and E_{Hxc} is the Hartree and exchange-correlation energy. The sum over i runs on the occupied states (up and down spins). The explicit form of $V_{\rm NL}$ is given in Ref. 13. The charge density is a quadratic functional of the orbitals: $\rho(\mathbf{r})=\Sigma_i\langle\psi_i|K(\mathbf{r})|\psi_i\rangle$ where the operator $K(\mathbf{r})$ is defined through augmentation functions which are localized on the atomic sites s.[13] The orbitals $|\psi_i\rangle$ satisfy the generalized orthogonality constraint $\langle\psi_i|S|\psi_j\rangle=\delta_{ij}$ where S is an overlap matrix which depends on the atomic positions. The orbitals are the solution of the generalized Kohn-Sham equations $H|\psi_i\rangle=\epsilon_i S|\psi_i\rangle$ with $H=-\frac{1}{2}\nabla^2+V_{KS}$ and $V_{KS}=\widetilde{V}_{NL}+V_{loc}+V_{Hxc}$. Here $\widetilde{V}_{NL}$ indicates the screened nonlocal potential (see Ref. 13) and V_{Hxc} is the Hartree and exchange-correlation potential.

The dynamical matrix at an arbitrary $\mathbf{q}$ point of the Brillouin zone (BZ) is the Fourier transform of the interatomic force constants $\mathbf{\Phi}_{s,s'}$. Within the adiabatic approximation, we can identify $\mathbf{\Phi}_{s,s'}$ with the mixed second derivatives of the total energy with respect to the displacements $\mathbf{u}_s$ and $\mathbf{u}_{s'}$ of the atoms at sites s and s'. Following the lines of Ref. 4 and taking the derivative of the Hellmann-Feynman forces, we find that the electronic contribution to $\mathbf{\Phi}_{s,s'}$ is composed of four terms. The first one, $\mathbf{\Phi}^{(1)}_{s,s'}$, corresponds to the expectation value of the second derivative of the electron-ion potential:

$$\mathbf{\Phi}^{(1)}_{s,s'}=\sum_i\left\langle\psi_i\left|\left[\frac{\partial^2(\widetilde{V}_{NL}+V_{loc})}{\partial\mathbf{u}_s\partial\mathbf{u}_{s'}}-\epsilon_i\frac{\partial^2 S}{\partial\mathbf{u}_s\partial\mathbf{u}_{s'}}\right]\right|\psi_i\right\rangle, \tag{1}$$

where the second derivative of $\widetilde{V}_{NL}$ is performed at fixed charge density. The second term $\mathbf{\Phi}^{(2)}_{s,s'}$ is

$$\mathbf{\Phi}^{(2)}_{s,s'}=\sum_i\left[\left\langle\frac{\partial\psi_i}{\partial\mathbf{u}_s}\right|P_c^+\left|\phi_{s',i}\right\rangle+\text{H.c.}\right], \tag{2}$$

where $P_c^+=1-\Sigma_i S|\psi_i\rangle\langle\psi_i|$ is the projector on the conduction-band subspace, H.c. indicates the hermitian conjugate, $|\phi_{s',i}\rangle=[\partial(\widetilde{V}_{NL}+V_{loc})/\partial\mathbf{u}_{s'}-\epsilon_i(\partial S/\partial\mathbf{u}_{s'})]|\psi_i\rangle$, and again the derivative of $\widetilde{V}_{NL}$ is performed at fixed density. In the normconserving PP scheme, the electronic contribution to $\mathbf{\Phi}_{s,s'}$ is simply given by the sum of $\mathbf{\Phi}^{(1)}_{s,s'}$ and $\mathbf{\Phi}^{(2)}_{s,s'}$, calculated for $S=1$ and $K(\mathbf{r})=|\mathbf{r}\rangle\langle\mathbf{r}|$.

In the ultrasoft PP scheme one must consider two additional contributions to $\mathbf{\Phi}_{s,s'}$ which have no corresponding counterparts in the normconserving scheme. $\mathbf{\Phi}^{(3)}_{s,s'}$ is the interaction between the change of the augmentation charge $\Delta_{s'}\rho(\mathbf{r})$ due to the atomic displacement $\mathbf{u}_{s'}$ [see Eq. (7) below] and the change of V_{Hxc} due to the displacement $\mathbf{u}_s$ [see Eq. (13) in Ref. 4]:

$$\mathbf{\Phi}^{(3)}_{s,s'}=\frac{1}{2}\int d^3r\left[\frac{\partial V_{Hxc}(\mathbf{r})}{\partial\mathbf{u}_s}\Delta_{s'}\rho(\mathbf{r})+\text{H.c.}\right]. \tag{3}$$

Finally, $\mathbf{\Phi}^{(4)}_{s,s'}$ is analogous to $\mathbf{\Phi}^{(2)}_{s,s'}$ but with the projector on the conduction-states subspace replaced by that on the valence-state subspace. Since the perturbation formalism provides explicitly only $P_c|\partial\psi_i/\partial\mathbf{u}_s\rangle$, the valence-state component must be derived from the constraint imposed by the orthogonality condition:

$$\left\langle\frac{\partial\psi_i}{\partial\mathbf{u}_s}\right|S\left|\psi_j\right\rangle+\left\langle\psi_i\right|S\left|\frac{\partial\psi_j}{\partial\mathbf{u}_s}\right\rangle=-\left\langle\psi_i\left|\frac{\partial S}{\partial\mathbf{u}_s}\right|\psi_j\right\rangle, \tag{4}$$

and one obtains

$$\mathbf{\Phi}^{(4)}_{s,s'}=-\left[\sum_{i,j}\left\langle\psi_i\left|\frac{\partial S}{\partial\mathbf{u}_s}\right|\psi_j\right\rangle\langle\psi_j|\phi_{s',i}\rangle+\text{H.c.}\right]. \tag{5}$$

We note that in the normconserving scheme, the left-hand side of Eq. (4) vanishes since $S=1$ and the constraint (4) allows one to show that the contribution to $\mathbf{\Phi}_{s,s'}$ from the valence-states component of $|\partial\psi_i/\partial\mathbf{u}_s\rangle$ is zero. On the contrary, in the ultrasoft case, Eq. (4) is used to evaluate such a component in terms of the unperturbed orbitals, as given in Eq. (5).

The key ingredient to evaluate the dynamical matrix is $P_c|\partial\psi_i/\partial\mathbf{u}_s\rangle$, which can be determined, within first-order perturbation theory, by solving the linear system:

$$(H-\epsilon_i S)P_c\left|\frac{\partial\psi_i}{\partial\mathbf{u}_s}\right\rangle=-P_c^+\left[\frac{\partial V_{KS}}{\partial\mathbf{u}_s}-\epsilon_i\frac{\partial S}{\partial\mathbf{u}_s}\right]|\psi_i\rangle, \tag{6}$$

where

$$\left[\frac{\partial V_{KS}}{\partial\mathbf{u}_s}-\epsilon_i\frac{\partial S}{\partial\mathbf{u}_s}\right]|\psi_i\rangle=|\phi_{s,i}\rangle+\int d^3r\,\frac{\partial V_{Hxc}(\mathbf{r})}{\partial\mathbf{u}_s}K(\mathbf{r})|\psi_i\rangle.$$

Equation (6) is a self-consistent linear system where the perturbing term depends on the variation of the charge density $\partial\rho(\mathbf{r})/\partial\mathbf{u}_s$ through $\partial V_{Hxc}(\mathbf{r})/\partial\mathbf{u}_s$. $\partial\rho(\mathbf{r})/\partial\mathbf{u}_s$ is a functional of $P_c|\partial\psi_i/\partial\mathbf{u}_s\rangle$:

$$\frac{\partial\rho(\mathbf{r})}{\partial\mathbf{u}_s}=2\sum_i\left\langle\frac{\partial\psi_i}{\partial\mathbf{u}_s}\right|P_c^+K(\mathbf{r})\left|\psi_i\right\rangle+\Delta_s\rho(\mathbf{r}). \tag{7}$$

The term $\Delta_s\rho(\mathbf{r})$, peculiar to the ultrasoft scheme, has two contributions: $\Delta_s\rho(\mathbf{r})=\delta_s\rho(\mathbf{r})+\delta_s\rho_{orth}(\mathbf{r})$. The former term $\delta_s\rho(\mathbf{r})=\Sigma_i\langle\psi_i|\partial K(\mathbf{r})/\partial\mathbf{u}_s|\psi_i\rangle$, accounts for the displacement of the augmentation charge at fixed orbitals whereas the latter

$$\delta_s\rho_{orth}(\mathbf{r})=-\Sigma_{i,j}\langle\psi_i|\partial S/\partial\mathbf{u}_s|\psi_j\rangle\langle\psi_j|K(\mathbf{r})|\psi_i\rangle,$$

appears because of the orthogonality constraint, similar to the $\mathbf{\Phi}^{(4)}_{s,s'}$ term in the interatomic force constants.

The generalization of the above formalism to metallic systems can be done along the same lines as in Ref. 17. The presence of the occupation factors modifies the definition of the valence-states subspace and the terms $\delta_s\rho_{orth}(\mathbf{r})$ and $\mathbf{\Phi}^{(4)}_{s,s'}$ must be modified accordingly. $\delta_s\rho_{orth}(\mathbf{r})$ becomes

$$\delta_s\rho_{orth}(\mathbf{r})=-\sum_{i,j}[\theta_{F,i}\theta_{i,j}+\theta_{F,j}\theta_{j,i}]\left\langle\psi_i\left|\frac{\partial S}{\partial\mathbf{u}_s}\right|\psi_j\right\rangle\times\langle\psi_j|K(\mathbf{r})|\psi_i\rangle,$$

where the occupation factors $\theta_{F,i}$ are defined as in Ref. 17. The sum extends over all states but, in practice, it is limited by the occupation factors to a small energy range beyond the Fermi surface. A similar modification applies to the expression for $\mathbf{\Phi}^{(4)}_{s,s'}$.

TABLE I. Calculated equilibrium intermolecular distance and vibrational frequencies of the four molecules studied in this work. The angle α of the H_2O molecule at equilibrium is α=105°(104.5°)[103.9°]. Accurate LDA values from recent computations (Ref. 28) are reported in parentheses. Experimental values are reported in square brackets (Ref. 20). No anharmonic correction is included. All frequencies are in cm^{-1}.

	d (a.u.)	ω_1	ω_2	ω_3
CO($C_{\infty v}$)	2.130 (2.132) [2.132]	Σ 2180 (2151) [2143]	—	—
CO_2 ($D_{\infty v}$)	2.207 (2.198) [2.197]	Σ_g 1355 (1336) [1333]	Σ_u 2439 (2374) [2349]	Π_u 641 (648) [667]
H_2O (C_{2v})	1.848 (1.833) [1.813]	A_1 3632 (3698)[3657]	A_1 1527 (1534) [1595]	B_2 3751 (3812) [3756]
CH_4 (T_d)	2.084 (2.074) [2.053]	A_1 2916 (2954) [2917]	E 1469 (1473) [1534]	T_2 1241 (1244)[1306]
		T_2 3046 (3082)[3019]	—	—

We now apply the above approach to a few examples. All calculations are performed within the local-density approximation (LDA) for the exchange and correlation energy.

As a first test, we consider the four molecules CO, CO_2, H_2O, and CH_4 in order to check the ability of the method to describe localized $2p$ electrons and short C—O, C—H, and O—H bonds. These bonds are easily studied with methods based on localized orbitals, but recently there has been an increasing interest to describe them with PW's since they are important for catalytic reactions on metallic surfaces.[18] For short bonds the choice of the core radius of the ultrasoft PP is critical because it is important to minimize the error due to the overlap of the augmentation charges.[19] In Table I, we give the equilibrium bond lengths and vibrational frequencies calculated with the present approach. We used a supercell geometry with a cubic unit cell of 25 a.u. and periodic boundary conditions. A kinetic energy cutoff of 25 Ry for the wave functions and of 200 Ry for the charge density were used. These cutoffs ensure a convergence error less than 1% for the vibrational frequencies. As an additional test of our linear-response method, we verified that the calculated vibrational frequency of CO coincides with that obtained from the total energy vs internuclear distance curve (within 2 cm^{-1}). Comparisons with the experimental (previous LDA) values indicate that the bond lengths have an average error of 1% (0.4%), while the frequencies have an average error of 2.5% (1.2%). We note however that the experimental frequencies contain anharmonic effects which are not included in our calculation. When using experimental values corrected for anharmonic effects,[20] the average error increases to 5%.

As a second example, we consider the phonon dispersions of noble metals which, in addition to s electrons, have a filled outer d shell which strongly influences chemical and structural properties. It is well known that the phonon dispersions of these metals can be fitted with force-constant models.[27] However, force constants obtained in this way for the bulk cannot be transferred to other bonding configurations, for example, to surfaces or clusters. To this end, first-principles approaches are particularly suited, but the necessity of treating s and d electrons on an equal footing makes it difficult to apply fully *ab initio* calculations to these metals. The most critical case for a PW approach is copper because the maximum of the $3d$ wave function occurs at only 0.6 a.u. from the nucleus. In a study of copper dimers, Ballone and Galli[21] showed that a kinetic energy cutoff of 306 Ry was necessary to obtain converged results for a normconserving PP. More recently, several smooth PP's have been generated for copper, which allows one to use energy cutoffs ranging from 50 Ry (Ref. 22) to 72 Ry.[23] Within the ultrasoft

TABLE II. Calculated lattice constant, bulk modulus, frequency of the longitudinal acoustic mode at the X point of the Brillouin zone and its derivative with respect to the lattice constant of the noble metals. The experimental data are given in parentheses for comparison (Ref. 27).

	a_0 (a.u.)	B_0 (kbar)	ω^X_{LA} (cm^{-1})	$\frac{\partial \omega^X_{LA}}{\partial a_0} \left(\frac{\mathrm{cm}^{-1}}{\mathrm{a.u.}}\right)$
Cu	6.72 (6.81)	1659 (1380)	263 (245)	−256
Ag	7.56 (7.69)	1350 (1020)	188 (171)	−199
Au	7.66 (7.67)	1823 (1720)	154 (155)	− 172

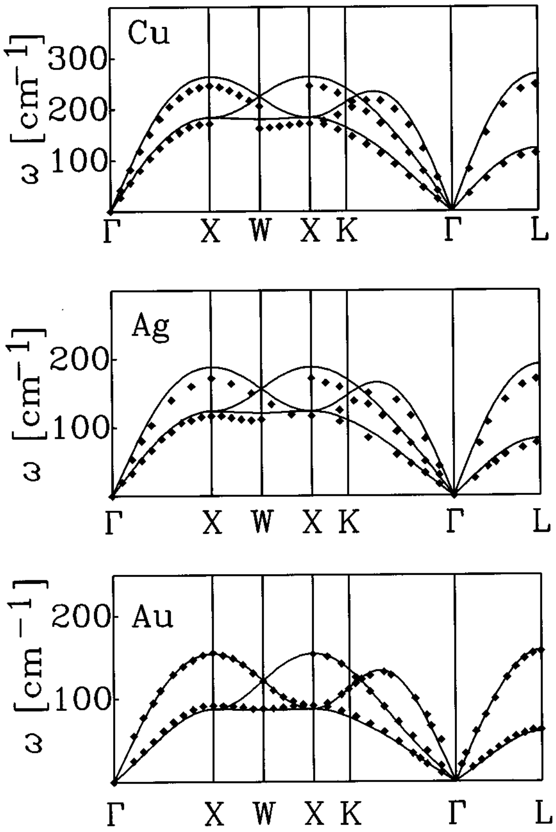

FIG. 1. Calculated phonon dispersions for fcc copper, silver, and gold (solid lines), compared with inelastic neutron-scattering data from Ref. 27 (solid diamonds).

scheme, the energy cutoff can be reduced to 20 Ry for the wave functions and 160 Ry for the charge density with a convergence error less than 1% on the frequencies. BZ integration has been performed with 408 special **k** points in the irreducible wedge with a smearing parameter $\sigma=0.02$ Ry.[17] The dynamical matrices were computed on a $4\times4\times4$ grid in **q** space. A Fourier interpolation technique provided the dynamical matrices at the other points of the BZ.[4]

In Table II, we report the fcc lattice constants and bulk moduli of the three metals obtained from a fit with the Murnaghan equation for the total energy as a function of volume. The equilibrium lattice constants of copper and silver are 1.3 and 1.7% smaller than their experimental values, while the bulk moduli are 20 and 30% higher. For gold we obtained the lowest errors: less than 0.5 and 6% for the lattice constant and the bulk modulus, respectively. Our calculated structural parameters agree well with recent results obtained with all-electron techniques.[24]

The calculated spectra are shown in Fig. 1, where they are compared with inelastic neutron-scattering data. Overall, good agreement is found between theory and experiment. For gold, the agreement is excellent all over the BZ. For copper and silver, the largest errors appear in the longitudinal acoustic branch at the *X* point. At this point, the theoretical values differ from experiment by 7% (Cu) and 9% (Ag). These differences should be correlated with the errors of the theoretical prediction of the lattice constant and bulk modulus. To illustrate the sensitivity of the phonon spectrum to the structural parameters, we also give in Table II the derivative of the frequency of the longitudinal acoustic mode at the *X* point with respect to the lattice constant. These derivatives correspond to Grüneisen parameters of 2.18 for copper and 2.67 for silver, in good agreement with the experimental BZ average of 1.97 and of 2.46, respectively.[25]

In conclusion we have extended DFPT for lattice dynamics to Vanderbilt's ultrasoft PP scheme. Our formulation opens the way for studies of the lattice dynamics of solids with large unit cells and containing localized electrons. Work is currently in progress to apply the present approach to small molecules adsorbed on metallic surfaces.[26]

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