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Linear response in a density-functional mixed-basis approach

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We present a generalization of density-functional based linear-response calculations of lattice dynamical properties to the case of general energy-independent basis sets. The formalism accounts for the nonorthogonality and atom-position dependence of the basis functions, and is suited for the application of norm-conserving pseudopotentials. We have implemented this scheme in the framework of a mixed-basis pseudopotential technique, which allows an efficient treatment of localized electrons. The accuracy of the present scheme is demonstrated by calculations of the phonon dispersions of the $4d$ metals Y and Ag. [S0163-1829(99)50930-2]

In recent years, density-functional perturbation theory (DFPT) (Refs. 1 and 2) has become a powerful tool for *ab initio* investigations of crystal properties related to external static perturbations of the electronic system. Applications of DFPT cover a broad spectrum of linear and nonlinear properties, ranging from harmonic phonon dispersions and eigenvectors, Born-effective charges,[2] dielectric permittivity to various anharmonic properties (nonlinear dipole coupling, Grüneisen parameters, and phonon linewidth[3,4]), and electron-phonon coupling,[5–7] and they also provide a parameter-free treatment of lattice thermodynamics.[8–10] While originally formulated for insulators, the method has been successfully extended to metallic systems.[11]

Until recently, the DFPT approach has been implemented for three different electronic structure methods. Most applications have been performed within the framework of a plane-wave basis set in conjunction with norm-conserving pseudopotentials, which is conceptually simple because the basis set does not depend on the external perturbation.[2,12,13] For solids containing localized electrons, as e.g., transition-metal compounds, the method requires a large number of plane waves, limiting its applicability to smaller system sizes. The other two DFPT implementations, which are based on linear muffin-tin orbital (LMTO) (Ref. 14) and linearized augmented plane-wave (LAPW) (Ref. 15) schemes, are better suited to describe localized electrons, as has been demonstrated in successful applications to perovskites and oxide compounds. However, for these all-electron methods, extensions to larger systems still remain a challenge.

Within the pseudopotential framework, there are two possible ways to improve the treatment of localized electrons with respect to the standard plane-wave approach: (i) modifying the pseudopotential, or (ii) modifying the basis set. The first one is realized by the ultrasoft pseudopotential (USPP) scheme, which allows a description of the valence orbitals by a rapidly converging plane-wave expansion, to the expense of dealing with a generalized orthogonality constraint for the orbitals, and of introducing augmentation charges in the core region. For this scheme, a DFPT formulation has been recently developed.[16]

The second approach employs a mixed-basis set for the description of the valence electrons.[17] It consists of localized functions centered at atomic sites which are chosen to optimize the description of the localized orbitals near an atomic site, and plane waves to account for the remaining smooth contributions of the wave functions. A proper choice of the localized functions can lead to a drastic reduction in the number of basis functions without sacrificing the accuracy. The efficiency and accuracy of total-energy and frozen-phonon calculations within this scheme has been demonstrated for a large variety of systems ranging from bulk and surface properties of transition-metal compounds to molecular crystals.[18–20] The disadvantages are technical complications due to the nonorthogonality of the basis set and the dependence of the localized functions on the atomic site, resulting in an enhanced complexity when dealing with perturbations, which up to now has prevented an implementation of DFPT within this scheme.

In this paper, we present an extension of the DFPT for lattice dynamics of solids to the case of a mixed-basis description of the wave functions. The present formulation is valid for a general energy-independent basis set, and can be used in conjunction with norm-conserving pseudopotentials. It accounts for possible nonorthogonality and atomic-position dependence of the basis functions, and is applicable to both insulating and metallic systems. We discuss the efficiency of the present method, and present results for the phonon spectra of two $4d$ transition metals with face-centered cubic (Ag) and hexagonal (Y) lattice structure.

In the Kohn-Sham scheme of DFT, the total energy of an insulating system is given as the sum of the ion-ion interaction and the electronic contribution (in Rydberg atomic units)

$$E_{el}=\sum_{i}^{occ}\{\langle\psi_i|T+v_{ion}|\psi_i\rangle\}+V_{HXC}[n(\mathbf{r})], \tag{1}$$

where $T=-\nabla^2$ denotes the kinetic operator. The electron-ion potential v_{ion} is represented by norm-conserving nonlocal pseudopotentials, and V_{HXC} denotes the Hartree and exchange-correlation contribution which is a functional of the electron density $n(\mathbf{r})=\Sigma_i^{occ}|\psi_i(\mathbf{r})|^2$. The single-particle wave functions $|\psi_i\rangle$ are the self-consistent solutions of the Kohn-Sham equation $H_{KS}|\psi_i\rangle=\epsilon_i|\psi_i\rangle$ with $H_{KS}=T+v_{ion}+v_{HXC}$ and $v_{HXC}[n(\mathbf{r})]=\delta V_{HXC}/\delta n(\mathbf{r})$.

In the following, we consider the general case of expanding the wave functions into an energy-independent basis set, $|\psi_i\rangle=\Sigma_\alpha c_\alpha(i)|\chi_\alpha\rangle$. The basis functions $|\chi_\alpha\rangle$ may be nonorthogonal and atom-position dependent, thus including the mixed-basis representation as a special case. The expansion coefficients $c_\alpha(i)$ are solutions of the generalized eigenvalue problem

$$\sum_\beta (H_{\alpha\beta}-\epsilon_i S_{\alpha\beta})c_\beta(i)=0 \tag{2}$$

with $H_{\alpha\beta}=\langle\chi_\alpha|H_{KS}|\chi_\beta\rangle$. The overlap matrix $S_{\alpha\beta}=\langle\chi_\alpha|\chi_\beta\rangle$ reflects the nonorthogonality of the basis set. The coefficients obey the generalized orthogonality constraint $\Sigma_{\alpha\beta}c_\alpha^*(i)S_{\alpha\beta}c_\beta(j)=\delta_{ij}$. Adopting a similar notation for the matrix elements of T and v_{ion}, the electronic part of the total energy takes the form:

$$E_{el}=\sum_i^{occ}\sum_{\alpha\beta} c_\alpha^*(i)(T_{\alpha\beta}+v_{\alpha\beta}^{ion})c_\beta(i)+V_{HXC}[n]. \tag{3}$$

Within the adiabatic approximation, lattice dynamical properties are accessible by considering a linear response of the electron system to a perturbation induced by atom displacements. A central quantity is the first-order variation of the valence charge density δn. In the mixed-basis scheme, δn is the sum of two terms, $\delta n=\delta n_{rigid}+\delta n_c$. The first one accounts for the rigid shift of the local basis functions and is given by $\delta n_{rigid}(\mathbf{r})=\Sigma_i^{occ}\Sigma_{\alpha\beta}c_\alpha^*(i)c_\beta(i)\delta(\chi_\alpha^*(\mathbf{r})\chi_\beta(\mathbf{r}))$. The second term describes the first-order response of the Kohn-Sham wave functions arising from changes in the expansion coefficients $c_\alpha(i)$. Similar to the case of a pure plane-wave basis,[1] it can be written as

$$\delta n_c(\mathbf{r})=2\sum_i^{occ}\sum_{\alpha\beta} c_\alpha^*(i)\chi_\alpha^*(\mathbf{r})\chi_\beta(\mathbf{r})(\Delta_\beta^H(i)-\Delta_\beta^S(i)), \tag{4}$$

where Δ^H is the solution of the linear equation

$$\sum_\beta (H_{\alpha\beta}-\epsilon_i S_{\alpha\beta})\Delta_\beta^H(i)=-\sum_{\beta\gamma} P_{\alpha\beta}^c\delta H_{\beta\gamma}c_\gamma(i) \tag{5}$$

and $P_{\alpha\beta}^c=\delta_{\alpha\beta}-\Sigma_j^{occ}\Sigma_\gamma S_{\alpha\gamma}c_\gamma^*(j)c_\beta(j)$ is the projector onto the conduction space. Due to the implicit dependence of H on the density, δH depends on δn leading to a self-consistent set of equations. The quantity Δ^S reflects the nonorthogonality of the basis functions and satisfies a linear equation similar to Eq. (5), but with δH replaced by δS, and the projector P^c replaced by

$$\begin{aligned}P_{\alpha\beta}^{(1)}&=\delta_{\alpha\beta}\epsilon_i-\sum_j^{occ}(\epsilon_i\Theta_{ij}+\epsilon_j\Theta_{ji})\sum_\gamma S_{\alpha\gamma}c_\gamma^*(j)c_\beta(j)\\&=\epsilon_i P_{\alpha\beta}^c+\sum_j^{occ}(\epsilon_i-\epsilon_j)\Theta_{ji}\sum_\gamma S_{\alpha\gamma}c_\gamma^*(j)c_\beta(j).\end{aligned} \tag{6}$$

Here, $\Theta_{ji}=\Theta(\epsilon_j-\epsilon_i)$, with Θ the Heaviside step function.

In harmonic approximation, phonons of wave vector $\mathbf{q}$ are described by the dynamical matrix, or equivalently, by the Fourier transform of the interatomic force constants Φ. The latter is given by the mixed second derivatives of the total energy with respect to atomic displacements of the form $u_{\mathbf{R}\kappa a}=U_{\kappa a}e^{i\mathbf{q}(\mathbf{R}+\mathbf{R}_\kappa)}+\text{c.c.}$

$$\Phi_{\kappa a\kappa' a'}(\mathbf{q})=\delta_{\kappa a}^-\delta_{\kappa' a'}^+E_{tot}. \tag{7}$$

Here, a and a' denote Cartesian coordinates, and we adopted the notation $\delta_{\kappa a}^-=\delta/\delta U_{\kappa a}^*$ and $\delta_{\kappa' a'}^+=\delta/\delta U_{\kappa' a'}$. When taking the derivatives, displacement induced changes in v_{ion} as well as in the local orbitals have to be taken into account. By straightforward differentiation of Eq. (3) we obtain three different contributions to Φ. The first contribution involves second derivatives of the matrix elements

$$\begin{aligned}\Phi_{\kappa a\kappa' a'}^{(1)}=\sum_i^{occ}\sum_{\alpha\beta} c_\alpha^*(i)(&\delta_{\kappa a}^-\delta_{\kappa' a'}^+H_{\alpha\beta}\\&-\epsilon_i\delta_{\kappa a}^-\delta_{\kappa' a'}^+S_{\alpha\beta})c_\beta(i).\end{aligned} \tag{8}$$

Here, the derivatives of H have to be taken at fixed charge density. Contrary to the plane-wave formalism, this expression also involves contributions from the matrix elements of T and v_{HXC} due to nonvanishing derivatives of the basis functions.

The second part of Φ is related to the first-order variation of the charge density via

$$\Phi_{\kappa a\kappa' a'}^{(2)}=\frac{1}{2}\int d^3r\,d^3r'\frac{\delta^2 V_{HXC}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\delta_{\kappa a}^-n(\mathbf{r})\delta_{\kappa' a'}^+n(\mathbf{r}'). \tag{9}$$

The third contribution to Φ contains the remaining terms involving first-order changes of the expansion coefficients. To write it in a compact form, it is convenient to split δH into a bare part obtained by keeping the charge density fixed, δH^b, and the part arising from the implicit dependence of H on the charge density,

$$\delta H_{\alpha\beta}^n=\int d^3r\langle\chi_\alpha|\frac{\delta v_{HXC}}{\delta n(\mathbf{r})}|\chi_\beta\rangle\delta n(\mathbf{r}). \tag{10}$$

Adopting a corresponding division of $\Delta^H=\Delta^b+\Delta^n$, we obtain

$$\begin{aligned}\Phi_{\kappa a\kappa' a'}^{(3)}=2\sum_i^{occ}\sum_{\alpha\beta}\{&\Delta_{\kappa a,\alpha}^b(i)^*\delta_{\kappa' a'}^+H_{\alpha\beta}^b c_\beta(i)\\&-\Delta_{\kappa a,\alpha}^n(i)^*\delta_{\kappa' a'}^+H_{\alpha\beta}^n c_\beta(i)\\&-\Delta_{\kappa a,\alpha}^S(i)^*\delta_{\kappa' a'}^+H_{\alpha\beta}^b c_\beta(i)\\&-c_\alpha^*(i)(\delta_{\kappa a}^-H_{\alpha\beta}^b)^*\Delta_{\kappa' a',\beta}^S(i)\\&+\Delta_{\kappa a,\alpha}^{S2}(i)^*\delta_{\kappa' a'}^+S_{\alpha\beta}c_\beta(i)\}.\end{aligned} \tag{11}$$

The last three terms represent corrections due to the nonorthogonality of the basis set. Δ^{S2} is related to a linear equa-

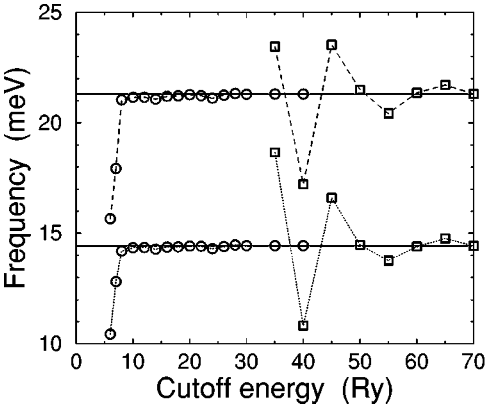

FIG. 1. Frequencies of the LA and TA phonons of Ag at the *X* point as a function of the cutoff energy for the plane-wave basis. Compared are results for calculations including (circles) and excluding (squares) local basis functions (dashed lines are guide to the eyes only). The two horizontal lines correspond to the converged mixed-basis results (14.44 meV for TA and 21.30 meV for LA, respectively).

tion similar to Δ^S, with the only modification that all ϵ factors in $P^{(1)}$ are replaced by corresponding ϵ^2 factors [Eq. (6)].

It is worth mentioning that only δH^n and Δ^n have to be updated in each iteration step of the self-consistent solution of δn, while all other terms have to be calculated only once. The present formulation corresponds to the stationary form of the mixed second derivatives (see Gonze and Lee[21]), which possesses the property that each component of Φ converges quadratically towards its self-consistent value, in the sense that its error is proportional to the square of the error of δn.

The generalization to metallic systems can be performed in a straightforward manner. As in the case of a pure plane-wave basis,[11] the introduction of fractional occupation numbers can be accounted for by a modification of the *P* matrices appearing in the linear equations for the quantities Δ, for example,

$$P^{(1)}_{\alpha\beta}=\delta_{\alpha\beta}\epsilon_i-\sum_j\,(\epsilon_i\tilde{\Theta}_{F,i}\tilde{\Theta}_{i,j}+\epsilon_j\tilde{\Theta}_{F,j}\tilde{\Theta}_{j,i})\times\sum_\gamma\,S_{\alpha\gamma}c^*_\gamma(j)c_\beta(j). \tag{12}$$

The occupation factors $\tilde{\Theta}_{F,i}$ are defined as in Ref. 11 and restrict the sum to states with energies slightly larger than the Fermi energy.

TABLE I. Calculated bulk properties of Ag and Y. Experimental values are given in parentheses.

Element	a (Å)	c/a	B (Mbar)	dB/dP
Ag	4.11 (4.09[a])	-	1.052 (0.997[b])	5.5
Y	3.58 (3.65[a])	1.570 (1.571[a])	0.460 (0.47[b])	3.5

[a] Reference 30.

[b] Reference 31.

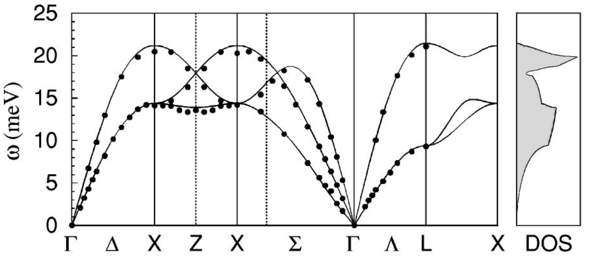

FIG. 2. Theoretical phonon dispersions and density of states for Ag. Experimental room temperature data (dots) are taken from Ref. 28.

We note that for metallic systems at $\mathbf{q}=0$ a first-order change in the chemical potential may occur which results in additional contributions to δn and Φ. It vanishes for perturbations which do not preserve the symmetry of the lattice, and is therefore of relevance only for totally symmetric phonon modes.

We have implemented the present formulation for the mixed-basis scheme[22] and have applied it to the calculation of phonon spectra for the two elemental metals Ag and Y. The calculations were carried out in the local-density approximation using the Hedin-Lundqvist form of the exchange-correlation functional.[23] The electron-core interaction is represented by norm-conserving pseudopotentials of the Hamann-Schlüter-Chiang type,[24] which have been used successfully in previous studies.[25,26] For Y, the $4p$ electrons have been treated as valence electrons to ensure a sufficient transferability of the pseudopotential.[26] Correspondingly, we have used eight local functions of *p* and *d* type with radial cutoffs of 2.6 a.u. For Ag, five local functions of *d* type have been employed with a cutoff of 2.7 a.u.

To demonstrate the efficiency of the mixed-basis approach, we present in Fig. 1 results for the convergence of the *X*-point phonon frequencies of Ag with respect to the cutoff energy of the plane-wave basis. These calculations have been performed for fixed lattice constants ($a=4.1$ Å) and for fixed number of *k* points in the Brillouin zone (BZ) integration (60 special points in the irreducible wedge). To obtain frequencies converged up to 0.5 meV, the use of a pure plane-wave basis requires a cutoff of at least 60 Ry. When the local *d*-type basis functions are employed, the same accuracy is reached already with a cutoff energy of 8 Ry, reducing the number of basis functions from 932 to 60. This drastically reduces the numerical effort for solving the linear equations [e.g., Eq. (5)], which represents the most time-consuming step of the algorithm.

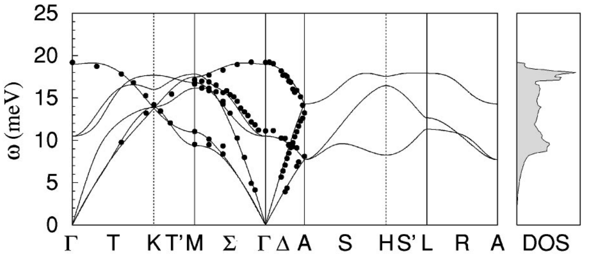

FIG. 3. Theoretical phonon dispersions and density of states for Y. Experimental room temperature data (dots) are taken from Ref. 29.

For the calculation of the whole phonon spectra, we have used a plane-wave cutoff energy of 16 Ry and 60 special k points in the irreducible wedge of the fcc BZ for Ag (512 points in the whole BZ). For Y, the corresponding values are 12 Ry and 76 k points in the irreducible wedge of the hexagonal BZ (1152 points in the whole BZ). The smearing technique with a Gaussian broadening of 0.2 eV has been applied in both cases.[27] Corresponding bulk properties are presented in Table I, which have been obtained by a fit to the Murnaghan equation of state. In the case of Y, the optimal lattice parameters are the results of an iterative optimization of the volume and the ratio c/a with respect to the total energy.

Phonon dispersions shown in Figs. 2 and 3 are obtained by standard Fourier interpolation method.[2,21] For this, force constants were calculated on a $4\times4\times4$ q-point grid for Ag and on a $6\times6\times4$ grid for Y. With this choice of parameters phonon frequencies were converged up to 0.2 meV. The results are in good agreement with available experimental data from inelastic neutron-scattering experiments.

The present mixed-basis scheme bears formal similarities to the USPP case, where the nonorthogonality of the wave functions and site dependent augmentation charges result in similar correction terms in the expressions for δn and Φ.[16] Both methods thus share a similar degree of complexity with respect to their implementations. While all types of norm-conserving pseudopotentials can be combined with the mixed-basis approach, the USPP method employs, by construction, pseudopotentials with potentially higher transferability. A more detailed comparison of the two approaches with respect to accuracy or performance is, however, not possible on the basis of presently available literature.

In summary we have presented a formulation of DFPT in the framework of a mixed-basis pseudopotential method. The combined use of plane waves and local orbitals provides an accurate and efficient treatment of the lattice dynamics of solids containing localized electrons.

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