

Sham, 1965). This approximation has turned out to be much more successful than originally expected (see, for instance, Jones and Gunnarsson, 1989), in spite of its extreme simplicity. For weakly correlated materials, such as semiconductors and simple metals, the LDA accurately describes structural and vibrational properties: the correct structure is usually found to have the lowest energy, while bond lengths, bulk moduli, and phonon frequencies are accurate to within a few percent.

The LDA also has some well-known drawbacks. A large overestimate ($\sim 20\%$) of the crystal cohesive and molecular binding energies is possibly the worst failure of this approximation, together with its inability to properly describe strongly correlated systems, such as transition-metal oxides. Much effort has been put into the search for better functionals than the LDA (see, for instance, Perdew *et al.*, 1999). The use of *gradient corrections* (Becke, 1988; Perdew *et al.*, 1996) to the LDA has become widespread in recent years. Gradient corrections are generally found to improve the account of electron correlations in finite or semi-infinite systems, such as molecules or surfaces; they are less helpful in infinite solids.

In general, DFT is a ground-state theory and Kohn-Sham eigenvalues and eigenvectors do not have a well-defined physical meaning. Nevertheless, for lack of better and equally general methods, Kohn-Sham eigenvalues are often used to estimate excitation energies. The features of the low-lying energy bands in solids obtained in this way are generally considered to be at least qualitatively correct, in spite of the fact that the LDA is known to substantially underestimate the optical gaps in insulators.

C. Linear response

In Sec. II.A, Eq. (10), we have seen that the electron-density linear response of a system determines the matrix of its interatomic force constants. Let us see now how this response can be obtained within density-functional theory. The procedure described in the following is usually referred to as *density-functional perturbation theory* (DFPT; Zein, 1984; Baroni *et al.*, 1987a; Gonze, 1995b).

In order to simplify the notation and make the argument more general, we assume that the external potential acting on the electrons is a differentiable function of a set of parameters, $\lambda \equiv \{\lambda_i\}$ ($\lambda_i \equiv \mathbf{R}_I$ in the case of lattice dynamics). According to the Hellmann-Feynman theorem, the first and second derivatives of the ground-state energy read

$$\frac{\partial E}{\partial \lambda_i} = \int \frac{\partial V_\lambda(\mathbf{r})}{\partial \lambda_i} n_\lambda(\mathbf{r}) d\mathbf{r}, \quad (21)$$

$$\frac{\partial^2 E}{\partial \lambda_i \partial \lambda_j} = \int \frac{\partial^2 V_\lambda(\mathbf{r})}{\partial \lambda_i \partial \lambda_j} n_\lambda(\mathbf{r}) d\mathbf{r} + \int \frac{\partial n_\lambda(\mathbf{r})}{\partial \lambda_i} \frac{\partial V_\lambda(\mathbf{r})}{\partial \lambda_j} d\mathbf{r}. \quad (22)$$

The electron-density response, $\partial n_\lambda(\mathbf{r})/\partial \lambda_i$, appearing in Eq. (22) can be evaluated by linearizing Eqs. (16), (15),

and (13) with respect to wave function, density, and potential variations. Linearization of Eq. (16) leads to

$$\Delta n(\mathbf{r}) = 4 \operatorname{Re} \sum_{n=1}^{N/2} \psi_n^*(\mathbf{r}) \Delta \psi_n(\mathbf{r}), \quad (23)$$

where the finite-difference operator Δ^λ is defined as

$$\Delta^\lambda F = \sum_i \frac{\partial F_\lambda}{\partial \lambda_i} \Delta \lambda_i. \quad (24)$$

The superscript λ has been omitted in Eq. (23), as well as in any subsequent formulas where such an omission does not give rise to ambiguities. Since the external potential (both unperturbed and perturbed) is real, each Kohn-Sham eigenfunction and its complex conjugate are degenerate. As a consequence, the imaginary part of the sum appearing in Eq. (23) vanishes, so that the prescription to keep only the real part can be dropped.

The variation of the Kohn-Sham orbitals, $\Delta \psi_n(\mathbf{r})$, is obtained by standard first-order perturbation theory (Messiah, 1962):

$$(H_{SCF} - \epsilon_n) |\Delta \psi_n\rangle = -(\Delta V_{SCF} - \Delta \epsilon_n) |\psi_n\rangle, \quad (25)$$

where

$$H_{SCF} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} + V_{SCF}(\mathbf{r}) \quad (26)$$

is the unperturbed Kohn-Sham Hamiltonian,

$$\Delta V_{SCF}(\mathbf{r}) = \Delta V(\mathbf{r}) + e^2 \int \frac{\Delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \left. \frac{dv_{xc}(n)}{dn} \right|_{n=n(\mathbf{r})} \Delta n(\mathbf{r}) \quad (27)$$

is the first-order correction to the self-consistent potential, and $\Delta \epsilon_n = \langle \psi_n | \Delta V_{SCF} | \psi_n \rangle$ is the first-order variation of the Kohn-Sham eigenvalue ϵ_n .

In the atomic physics literature, an equation analogous to Eq. (25) is known as the Sternheimer equation, after the work in which it was first used to calculate atomic polarizabilities (Sternheimer, 1954). A self-consistent version of the Sternheimer equation was introduced by Mahan (1980) to calculate atomic polarizabilities within density-functional theory in the LDA. Similar methods are known in the quantum chemistry literature under the generic name of *analytic evaluation of second-order energy derivatives* (Gerratt and Mills, 1968; Amos, 1987). In the specific context of the Hartree-Fock approximation, the resulting algorithm is called the *coupled Hartree-Fock method* (Gerratt and Mills, 1968).

Equations (23)–(27) form a set of self-consistent equations for the perturbed system completely analogous to the Kohn-Sham equations in the unperturbed case—Eqs. (13), (15), and (16)—with the Kohn-Sham eigenvalue equation, Eq. (15), being replaced by the solution of a linear system, Eq. (25). In the present case, the self-consistency requirement manifests itself in the dependence of the right-hand side upon the solution of the linear system. As $\Delta V_{SCF}(\mathbf{r})$ is a linear functional of

$\Delta n(\mathbf{r})$, which in turn depends linearly on the $\Delta\psi$'s, the whole self-consistent calculation can be cast in terms of a generalized linear problem. Note, however, that the right-hand side of Eq. (25) for $\Delta\psi_n$ depends through Δn on the solution of all the similar equations holding for the $\Delta\psi_m$ ($m \neq n$). Hence all the N equations, Eq. (25), are linearly coupled to each other, and the set of all the $\Delta\psi$'s is the solution of a linear problem whose dimension is $(NM/2 \times NM/2)$, M being the size of the basis set used to describe the ψ 's. The explicit form of this big linear equation can be worked out directly from Eqs. (23)–(27), or it can equivalently be derived from a variational principle, as explained in Sec. II.C.3. Whether this large linear system is better solved directly by iterative methods or by the self-consistent solution of the smaller linear systems given by Eq. (25) is a matter of computational strategy.

The first-order correction to a given eigenfunction of the Schrödinger equation, given by Eq. (25), is often expressed in terms of a sum over the spectrum of the unperturbed Hamiltonian,

$$\Delta\psi_n(\mathbf{r}) = \sum_{m \neq n} \psi_m(\mathbf{r}) \frac{\langle \psi_m | \Delta V_{SCF} | \psi_n \rangle}{\epsilon_n - \epsilon_m} \quad (28)$$

running over all the states of the system, occupied and empty, with the exception of the state being considered, for which the energy denominator would vanish. Using Eq. (28), the electron charge-density response, Eq. (23), can be cast into the form

$$\Delta n(\mathbf{r}) = 4 \sum_{n=1}^{N/2} \sum_{m \neq n} \psi_n^*(\mathbf{r}) \psi_m(\mathbf{r}) \frac{\langle \psi_m | \Delta V_{SCF} | \psi_n \rangle}{\epsilon_n - \epsilon_m}. \quad (29)$$

Equation (29) shows that the contributions to the electron-density response coming from products of occupied states cancel each other, so that the m index can be thought of as attaching to conduction states only. This is equivalent to saying that the electron-density distribution does not respond to a perturbation, which acts only on the occupied-state manifold (or, more generally, to the component of any perturbation which couples occupied states among each other).

The explicit evaluation of $\Delta\psi_n(\mathbf{r})$ from Eq. (28) would require a knowledge of the full spectrum of the Kohn-Sham Hamiltonian and extensive summations over conduction bands. In Eq. (25), instead, only knowledge of the occupied states of the system is needed to construct the right-hand side of the equation, and efficient iterative algorithms—such as the conjugate gradient (Press *et al.*, 1989; Stich *et al.*, 1989; Payne *et al.*, 1992) or minimal residual (Press *et al.* 1989; Saad and Schultz, 1986) methods—can be used for solution of the linear system. In this way the computational cost of determining of the density response to a single perturbation is of the same order as that needed to calculate the unperturbed ground-state density.

The left-hand side of Eq. (25) is singular because the linear operator appearing therein has a null eigenvalue. However, we saw above that the response of the system

to an external perturbation depends only on the component of the perturbation that couples the occupied-state manifold with the empty-state one. The projection onto the empty-state manifold of the first-order correction to occupied orbitals can be obtained from Eq. (25) by replacing its right-hand side with $-P_c \Delta V_{SCF} | \psi_n \rangle$, where P_c is the projector onto the empty-state manifold, and by adding to the linear operator on its left-hand side $H_{SCF} - \epsilon_n$, a multiple of the projector onto the occupied-state manifold, P_v , so as to make it nonsingular:

$$(H_{SCF} + \alpha P_v - \epsilon_n) | \Delta \psi_n \rangle = -P_c \Delta V_{SCF} | \psi_n \rangle. \quad (30)$$

In practice, if the linear system is solved by the conjugate-gradient or any other iterative method and the trial solution is chosen orthogonal to the occupied-state manifold, orthogonality is maintained during iteration without regard for the extra P_v term on the left-hand side of Eq. (30).

The above discussion applies to insulators in which the gap is finite. In metals a finite density of states (DOS) occurs at the Fermi energy, and a change in the orbital occupation number may occur upon the application of an infinitesimal perturbation. The modifications of DFPT needed to treat the linear response of metals have been discussed by de Gironcoli (1995) and will be presented in some detail in Sec. II.C.4.

1. Monochromatic perturbations

One of the greatest advantages of DFPT—as compared to other nonperturbative methods for calculating the vibrational properties of crystalline solids (such as the frozen-phonon or molecular-dynamics spectral analysis methods)—is that within DFPT the responses to perturbations of different wavelengths are decoupled. This feature allows one to calculate phonon frequencies at arbitrary wave vectors \mathbf{q} avoiding the use of supercells and with a workload that is essentially independent of the phonon wavelength. To see this in some detail, we first rewrite Eq. (30) by explicitly indicating the wave vector \mathbf{k} and band index v of the unperturbed wave function $\psi_v^{\mathbf{k}}$, and by projecting both sides of the equation over the manifold of states of wave vector $\mathbf{k} + \mathbf{q}$. Translational invariance requires that the projector onto the $\mathbf{k} + \mathbf{q}$ manifold, $P^{\mathbf{k} + \mathbf{q}}$, commute with H_{SCF} and with the projectors onto the occupied- and empty-state manifolds, P_v and P_c . By indicating with $P^{\mathbf{k} + \mathbf{q}} P_v = P_v^{\mathbf{k} + \mathbf{q}}$ and $P^{\mathbf{k} + \mathbf{q}} P_c = P_c^{\mathbf{k} + \mathbf{q}}$ the projectors onto the occupied and empty states of wave vector $\mathbf{k} + \mathbf{q}$, one can rewrite Eq. (30) as

$$(H_{SCF} + \alpha P_v^{\mathbf{k} + \mathbf{q}} - \epsilon_v^{\mathbf{k}}) | \Delta \psi_v^{\mathbf{k} + \mathbf{q}} \rangle = -P_c^{\mathbf{k} + \mathbf{q}} \Delta V_{SCF} | \psi_v^{\mathbf{k}} \rangle, \quad (31)$$

where $| \Delta \psi_v^{\mathbf{k} + \mathbf{q}} \rangle = P^{\mathbf{k} + \mathbf{q}} | \Delta \psi_v^{\mathbf{k}} \rangle$. When one decomposes the perturbing potential ΔV_{SCF} into Fourier components,

$$\Delta V_{SCF}(\mathbf{r}) = \sum_{\mathbf{q}} \Delta v_{SCF}^{\mathbf{q}}(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}}, \quad (32)$$