Linear-Response Calculations of Lattice Dynamics Using Muffin-Tin Basis Sets

S. Yu. Savrasov[a]

Max-Planck-Institute für Festkörperforschung, D-7000 Stuttgart 80, Germany

(Received 13 July 1992)

An all-electron formulation of density-functional linear-response theory is presented. It is based on representing the first-order corrections to the one-electron wave functions in terms of a muffin-tin basis set. This, for instance, makes *ab initio* calculations of lattice dynamics for transition-metal systems possible. The computability is demonstrated for phonon dispersions in Nb and the results are found to be in excellent agreement with frozen-phonon calculations and with experimental data.

PACS numbers: 71.10.+x, 63.20.Dj, 77.90.+k

In recent years, the density-functional (DF) approach [1] to the linear-response problem has proved to be a powerful method for determining various solid-state properties. These include static dielectric properties in semiconductors and ionic crystals [2], screening response to electric fields and point charges [3], as well as lattice dynamical properties [4–7].

The problem for calculating the lattice dynamics essentially amounts to finding the *change* of the electronic charge density induced by the presence of a phonon with wave vector $\mathbf{q}$. To date the most efficient technique developed for calculating this quantity is the solid-state generalization [4] of the Sternheimer method [8]. In this method, the external perturbation $\delta V_{\rm ext}$ caused by the proton displacements $\delta\mathbf{R}=\mathbf{d}e^{i\mathbf{q}\cdot\mathbf{R}}+\mathbf{d}^*e^{-i\mathbf{q}\cdot\mathbf{R}}$ ($\mathbf{d}$ is the polarization vector) is static, real, and can be represented as the sum of two components: $\delta V_{\rm ext}=\delta^+V_{\rm ext}+\delta^-V_{\rm ext}$. Both components are Hermitian, i.e., $(\delta^+V_{\rm ext})^*=\delta^-V_{\rm ext}$ and they translate like Bloch waves with wave vectors $+\mathbf{q}$ and $-\mathbf{q}$ in the Brillouin zone of the unperturbed crystal. The first-order change of the charge density $\delta\rho$ can be represented in the same form as $\delta V_{\rm ext}$, i.e., $\delta\rho=\delta^+\rho+\delta^-\rho$, and is expressed in terms of the one-electron wave functions $\psi_{\mathbf{k}\lambda}$ and their first-order corrections $\delta^+\psi_{\mathbf{k}\lambda}$ and $\delta^-\psi_{\mathbf{k}\lambda}$ as follows: $\delta^\pm\rho=\sum f_{\mathbf{k}\lambda}(\delta^\pm\psi^*_{\mathbf{k}\lambda}\psi_{\mathbf{k}\lambda}+\psi^*_{\mathbf{k}\lambda}\times\delta^\pm\psi_{\mathbf{k}\lambda})$, where $\delta^\pm\psi^*_{\mathbf{k}\lambda}=(\delta^\mp\psi_{\mathbf{k}\lambda})^*$. Here $f_{\mathbf{k}\lambda}$ are the occupation numbers and λ numerates the bands. The first-order correction $|\delta^\pm\mathbf{k}\lambda\rangle\equiv\delta^\pm\psi_{\mathbf{k}\lambda}$ is a Bloch state with wave vector $\mathbf{k}\pm\mathbf{q}$ and is the solution of the so-called Sternheimer equation, which is the Schrödinger equation to linear order:

$$(H-E_{\mathbf{k}\lambda})|\delta^\pm\mathbf{k}\lambda\rangle+\delta^\pm V|\mathbf{k}\lambda\rangle=0\,, \tag{1}$$

where $H\equiv-\nabla^2+V$ is the unperturbed one-electron Hamiltonian. Equation (1) must be solved self-consistently since the induced charge density expressed via $|\delta^\pm\mathbf{k}\lambda\rangle$ screens out the external field $\delta^\pm V_{\rm ext}$. Therefore, it is the screened perturbation $\delta^\pm V$ which appears in Eq. (1). There, we have also projected onto periodicity $\mathbf{k}\pm\mathbf{q}$ and dropped the term $\delta^\pm E_{\mathbf{k}\lambda}|\mathbf{k}\lambda\rangle$.

This method has the following advantages: It is *not* limited to $\mathbf{q}$'s commensurate with the lattice as is the frozen-phonon supercell approach and it does not use *all* the Bloch states of the unperturbed crystal as a basis for representing $|\delta^\pm\mathbf{k}\lambda\rangle$ as it is done in the perturbative approach [9].

The construction of a rapidity convergent basis set for representing the first-order corrections is important because $|\mathbf{k}\lambda\rangle$ and $|\delta^\pm\mathbf{k}\lambda\rangle$ oscillate in the core region. To date, most calculations of phonon dispersions have been done for broad-band semiconductors and insulators [5], where this problem can be eliminated by the pseudopotential approximation. The latter allows the use of plane-wave basis sets. Unfortunately, with decreasing bandwidth, the plane-wave expansion of the pseudo wave functions converges more slowly and it becomes less advantageous to use pseudopotentials. Indeed, until most recently [6,7], the literature contains no *ab initio* calculations of phonon dispersions for *transition-metal systems* [10].

In the present Letter, I propose an efficient all-electron approach. The first-order corrections are represented in terms of *muffin-tin-(MT) basis sets* such as linear muffin-tin orbitals (LMTO) or linear augmented plane waves (LAPW) [11]. The important advantage of such a formulation is that it treats narrow-band systems on the same footing as the wide-band systems. The method is also fast and accurate: The time required to calculate the dynamical matrix for an arbitrary $\mathbf{q}$ vector is about the same as that required to perform a self-consistent band-structure calculation for the unperturbed crystal; the accuracy of calculated phonon frequencies is a few percent.

There are two problems connected with the use of MT basis functions in the linear-response method. The first problem is that the unperturbed energy bands $E_{\mathbf{k}\lambda}$ and wave functions $|\mathbf{k}\lambda\rangle$ are obtained in this basis by applying the Rayleigh-Ritz variational principle. They are *not exact* solutions of the one-electron Schrödinger equation. Consequently, a variational formulation for the linear response is also necessary. The second problem is that the MT basis functions are tailored to the unperturbed one-electron potential and must therefore be reconstructed to take into account the specifics of the perturbation. In particular, the partial-wave augmentation inside the MT spheres must follow by the atomic movements.

The first problem is to find an energy functional the minimization of which with respect to $|\delta^\pm\mathbf{k}\lambda\rangle$ leads to

the solution of Eq. (1). This functional can be obtained by expanding the total energy with respect to the change in the external potential up to second order,

$$d^2E=\sum_{\mathbf{k}\lambda} f_{\mathbf{k}\lambda}(\langle\delta^+\delta^-\mathbf{k}\lambda+\delta^-\delta^+\mathbf{k}\lambda|H-E_{\mathbf{k}\lambda}|\mathbf{k}\lambda\rangle+2\langle\delta^+\mathbf{k}\lambda|H-E_{\mathbf{k}\lambda}|\delta^+\mathbf{k}\lambda\rangle)$$
$$+\int\delta^+\rho\delta^-V+\int\delta^+\rho\delta^-V_{\text{ext}}+\int\rho\delta^+\delta^-V_{\text{ext}}+\text{c.c.}\,, \tag{2}$$

where $|\delta^\pm\delta^\mp\mathbf{k}\lambda\rangle$ denote second-order corrections to the wave functions and where $\delta^+\delta^-V_{\text{ext}}$ is the second-order change in the bare nuclear potential due to atomic displacements [12]. This expression is the second-order change in the DF total energy (its electronic part) and is directly interpreted as the electronic contribution to the dynamical matrix. (Its nuclear part is the Ewald contribution which is evaluated trivially.) d^2E is *variational* with respect to the first-order changes in wave functions just like the unperturbed total energy is variational with respect to unperturbed states $|\mathbf{k}\lambda\rangle$. This property of the density functional follows from the Hohenberg-Kohn variational principle and allows us to estimate the dynamical matrix quite precisely: While the first-order changes in the wave functions and the charge densities are only variationally accurate, the error will be of the second order with respect to the error in $|\delta^\pm\mathbf{k}\lambda\rangle$. The expression (2) in its minimum contains no second and third terms and may therefore be interpreted as the Hellmann-Feynman result (last two terms there) plus incomplete-basis-set (IBS) correction [first contribution in (2)]. The latter is due to approximate character of unperturbed states $|\mathbf{k}\lambda\rangle$. The IBS term is the analog of the "Pulay force" known in atomic force calculations [13].

The second problem is to construct a specific Hilbert space for representing the first-order corrections. Let us first specify the MT basis set $\{|\chi_\alpha^{\mathbf{k}}\rangle\}$ with the size N used to expand the unperturbed functions $|\mathbf{k}\lambda\rangle$: Space is partitioned into atom-centered MT spheres and the interstitial region. Within the spheres the MT orbitals are defined as linear combinations of numerical radial functions multiplied by spherical harmonics. In the interstitial region these quantities can be, for instance, spherical Hankel functions, as in the LMTO method, or plane waves as in the LAPW method. The numerical radial functions are the regular solutions of the radial Schrödinger equation for the spherical part of the potential at an energy E_ν at the center of interest, as well as the energy derivatives of these functions. The one-electron wave function is represented as the linear combination $|\mathbf{k}\lambda\rangle=\sum_\alpha^N|\chi_\alpha^{\mathbf{k}}\rangle A_\alpha^{\mathbf{k}\lambda}$, where $A_\alpha^{\mathbf{k}\lambda}$ are the expansion coefficients found from the matrix eigenvalue problem: $\sum_\alpha^N\langle\chi_\beta^{\mathbf{k}}|H-E_{\mathbf{k}\lambda}|\chi_\alpha^{\mathbf{k}}\rangle A_\alpha^{\mathbf{k}\lambda}=0$. (The one-electron Hamiltonian H may include nonspherical terms of the potential.)

In the linear-response calculation, the first-order change $|\delta^\pm\mathbf{k}\lambda\rangle$ must include the change $|\delta^\pm\chi_\alpha^{\mathbf{k}}\rangle$ in the *Bloch* MT basis set as well as change $\delta^\pm A_\alpha^{\mathbf{k}\lambda}$ in the expansion coefficients, i.e.,

$$|\delta^\pm\mathbf{k}\lambda\rangle=\sum_\alpha^N(|\delta^\pm\chi_\alpha^{\mathbf{k}}\rangle A_\alpha^{\mathbf{k}\lambda}+|\chi_\alpha^{\mathbf{k}\pm\mathbf{q}}\rangle\delta^\pm A_\alpha^{\mathbf{k}\lambda})\,. \tag{3}$$

Since $|\delta^\pm\mathbf{k}\lambda\rangle$ is a Bloch state of wave vector $\mathbf{k}\pm\mathbf{q}$, so are $|\delta^\pm\chi_\alpha^{\mathbf{k}}\rangle$ and $|\chi_\alpha^{\mathbf{k}\pm\mathbf{q}}\rangle$. The latter is the original basis function of wave vector $\mathbf{k}\pm\mathbf{q}$ and the former is constructed as follows: Inside the MT spheres, the basis $|\delta^\pm\chi_\alpha^{\mathbf{k}}\rangle$ is represented by the change in the numerical radial functions plus a term connected with the change in the structure constants, specifically, in the LMTO-based methods. The change in the radial functions is described by a set of inhomogeneous (uncoupled) differential equations obtained by linearizing the radial Schrödinger equations with respect to $\delta^\pm V$ [6]. It contains two contributions: the first, trivial one, connected with the *rigid* movement of the potential, and the second, connected with the change in the shape of the potential. In the interstitial region, the basis $|\delta^\pm\chi_\alpha^{\mathbf{k}}\rangle$ is zero in the LAPW method, and in the LMTO method it is given by the sum $\sum_{\mathbf{R}}e^{i(\mathbf{k}\pm\mathbf{q})\cdot\mathbf{R}}\nabla h_L(\mathbf{r}-\mathbf{R})$ of spherical Hankel functions h_L centered at sites $\mathbf{R}$ of the lattice. The expansion of $|\delta^\pm\mathbf{k}\lambda\rangle$ written in the form (3) is fastly convergent because the basis $|\delta^\pm\chi_\alpha^{\mathbf{k}}\rangle$, by construction, is adjusted to the perturbation just like the original basis $|\chi_\alpha^{\mathbf{k}}\rangle$ is adjusted to the unperturbed one-electron potential. Equation (3) can be interpreted as the representation of $|\delta^\pm\mathbf{k}\lambda\rangle$ in terms of $|\chi_\alpha^{\mathbf{k}\pm\mathbf{q}}\rangle$ in the local coordinate system displaced together with the nucleus; the convergence with respect to the number of orbitals per atom in (3) must be about the same as for the unperturbed states.

The second-order changes $|\delta^\pm\delta^\mp\mathbf{k}\lambda\rangle$ must also be considered. They appear in this formulation of the problem because the states $|\mathbf{k}\lambda\rangle$ are not exact, but merely variational solutions [see first term in (2)]. This second-order variation of the wave functions is

$$|\delta^\pm\delta^\mp\mathbf{k}\lambda\rangle=\sum_\alpha^N(|\chi_\alpha^{\mathbf{k}}\rangle\delta^\pm\delta^\mp A_\alpha^{\mathbf{k}\lambda}+|\delta^\mp\chi_\alpha^{\mathbf{k}\pm\mathbf{q}}\rangle\delta^\pm A_\alpha^{\mathbf{k}\lambda}+|\delta^\pm\chi_\alpha^{\mathbf{k}\mp\mathbf{q}}\rangle\delta^\mp A_\alpha^{\mathbf{k}\lambda}+|\delta^\pm\delta^\mp\chi_\alpha^{\mathbf{k}}\rangle A_\alpha^{\mathbf{k}\lambda})\,, \tag{4}$$

where $\delta^\pm\delta^\mp A_\alpha^{\mathbf{k}\lambda}$ and $|\delta^\pm\delta^\mp\chi_\alpha^{\mathbf{k}}\rangle$ are the second-order changes in the expansion coefficients and the basis functions, respectively. Inserting this definition into Eq. (2) one realizes that the second-order changes in $A_\alpha^{\mathbf{k}\lambda}$ disappear because they enter the functional only as coefficients of the unperturbed basis functions. The last three contributions in Eq. (4), on the other hand, are important for evaluating d^2E.

Having fixed the Hilbert space $\{|\chi\rangle;|\delta\chi\rangle\}$ of the basis functions, we now see that the variational freedom of the functional (2) is provided only by the coefficients $\delta^{\pm}A_{\alpha}^{\mathbf{k}\lambda}$. Let us minimize d^2E with respect to $\delta^{\pm}A_{\alpha}^{\mathbf{k}\lambda}$. We obtain

$$\sum_{\alpha}^{N}\langle\chi_{\beta}^{\mathbf{k}\pm\mathbf{q}}|H-E_{\mathbf{k}\lambda}|\chi_{\alpha}^{\mathbf{k}\pm\mathbf{q}}\rangle\delta^{\pm}A_{\alpha}^{\mathbf{k}\lambda}+\sum_{\alpha}^{N}(\langle\chi_{\beta}^{\mathbf{k}\pm\mathbf{q}}|\delta^{\pm}V|\chi_{\alpha}^{\mathbf{k}}\rangle+\langle\delta^{\pm}\chi_{\beta}^{\mathbf{k}\mp\mathbf{q}}|H-E_{\mathbf{k}\lambda}|\chi_{\alpha}^{\mathbf{k}}\rangle+\langle\chi_{\beta}^{\mathbf{k}\pm\mathbf{q}}|H-E_{\mathbf{k}\lambda}|\delta^{\pm}\chi_{\alpha}^{\mathbf{k}}\rangle)A_{\alpha}^{\mathbf{k}\lambda}=0. \quad (5)$$

This linear system of equations determines the position of the minimum of d^2E in the space of the coefficients $\delta^{\pm}A_{\alpha}^{\mathbf{k}\lambda}$, and all second-order changes, such as $|\delta^{\pm}\delta^{\mp}\chi_{\alpha}^{\mathbf{k}}\rangle$, do not affect it. The functions $|\delta^{\pm}\delta^{\mp}\chi_{\alpha}^{\mathbf{k}}\rangle$, on the other hand, define the value d^2E itself in its minimum and must be taken into account in the dynamical matrix evaluation.

We must now solve (5) for the coefficients $\delta^{\pm}A_{\alpha}^{\mathbf{k}\lambda}$. This is done by inverting the matrix $\langle\chi_{\beta}^{\mathbf{k}\pm\mathbf{q}}|H-E_{\mathbf{k}\lambda}|\chi_{\alpha}^{\mathbf{k}\pm\mathbf{q}}\rangle$, whose eigenvalues are $E_{\mathbf{k}\pm\mathbf{q}\lambda'}-E_{\mathbf{k}\lambda}$ and eigenvectors are $A_{\alpha}^{\mathbf{k}\pm\mathbf{q}\lambda'}$, $\lambda'=1,N$. The result for $\delta^{\pm}A_{\alpha}^{\mathbf{k}\lambda}$ is then substituted into (3) that gives the final expression for $|\delta^{\pm}\mathbf{k}\lambda\rangle$ in the form

$$|\delta^{\pm}\mathbf{k}\lambda\rangle=\sum_{\alpha}^{N}|\delta^{\pm}\chi_{\alpha}^{\mathbf{k}}\rangle A_{\alpha}^{\mathbf{k}\lambda}+\sum_{\lambda'}^{N}\frac{|\mathbf{k}\pm\mathbf{q}\lambda'\rangle}{E_{\mathbf{k}\lambda}-E_{\mathbf{k}\pm\mathbf{q}\lambda'}}\left(\langle\mathbf{k}\pm\mathbf{q}\lambda'|H-E_{\mathbf{k}\lambda}\left|\sum_{\alpha}^{N}\delta^{\pm}\chi_{\alpha}^{\mathbf{k}}A_{\alpha}^{\mathbf{k}\lambda}\right\rangle+\left\langle\sum_{\alpha}^{N}\delta^{\pm}\chi_{\alpha}^{\mathbf{k}\mp\mathbf{q}}A_{\alpha}^{\mathbf{k}\pm\mathbf{q}\lambda'}\right|H-E_{\mathbf{k}\lambda}|\mathbf{k}\lambda\rangle\right.$$
$$\left.+\langle\mathbf{k}\pm\mathbf{q}\lambda'|\delta^{\pm}V|\mathbf{k}\lambda\rangle\right). \quad (6)$$

This formula has a simple physical meaning. The first three terms containing $|\delta\chi\rangle$ appear because of the use of *variational* solutions. These can be interpreted as IBS corrections to the last term (the one with $\delta^{\pm}V$), which has the form of standard perturbation theory. If *all* unperturbed states $|\mathbf{k}\pm\mathbf{q}\lambda'\rangle$ are exact and they represent *mathematically* a complete basis set, then the first and second terms in (6) cancel each other and the third term also vanishes: We thus come back to the standard perturbative formula. However, the use of the functions $|\delta\chi\rangle$ in the basis greatly reduces the number of states $|\mathbf{k}\pm\mathbf{q}\lambda'\rangle$ needed to reach the convergence in (6). Namely, following the above derivation, the summation in the last three terms is over N energy states, N being the size of the basis for the *unperturbed* system. Furthermore, since the response can be found as a ground-state property of both perturbed and unperturbed systems, only the occupied states must be well reproduced; the excited states can, in principle, be arbitrary. The LMTO and LAPW methods are very suitable for this purpose: They are fast and accurate within a certain energy window. The states $|\mathbf{k}\pm\mathbf{q}\lambda'\rangle$ in (6) are the eigenstates of the Hamiltonian matrix $\langle\chi_{\beta}^{\mathbf{k}\pm\mathbf{q}}|H|\chi_{\alpha}^{\mathbf{k}\pm\mathbf{q}}\rangle$ which is itself constructed to reproduce the occupied bands well. (This is the energy window of our interest and all centers of linearization E_{ν} are placed in there.) Consequently, the excited states are not to be interpreted as the exact ones; only the knowledge of *occupied* energy bands is necessary in this linear-response formulation [14].

The method described above can, in principle, be applied to general perturbations. Below, a specific application to the transition-metal lattice dynamics is given and the results for phonon dispersions in bcc Nb calculated in ten equally spaced $\mathbf{q}$ points along the line $(2\pi/a)(0,0,1)$ are presented. I have generalized a recent version [15] of the full-potential LMTO method for these linear-response calculations. One-center spherical-harmonic expansions (up to $l_{\max}=8$) are used for all the relevant quantities including charge densities, potentials, and response functions. The LMTO basis $\{|\chi\rangle\}$ and its change $\{|\delta\chi\rangle\}$ include only s, p, and d orbitals per atom [$N=9$ in Eq. (6)]. The tetrahedron method of Ref. [16] is used for the integration over the Brillouin zone (BZ); both electron-phonon matrix elements and energy denominator in (6) are interpolated linearly within a polyhedron. The number of $\mathbf{k}$ points is equal to 91 (285 near the phonon anomalies) per $\frac{1}{48}$ th of the BZ. The lattice constant was taken to be $a=6.15$ a.u. as obtained by the LMTO total-energy calculation.

Figure 1 shows calculated longitudinal and transverse phonon branches for Nb. The results of the linear-response method (full lines) are compared with frozen-phonon supercell calculations performed independently with the full-potential LMTO method (circles) as well as with experiment [17] (triangles). We see that the

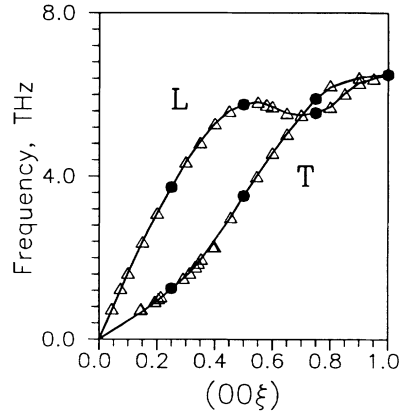

FIG. 1. Calculated phonon dispersions in Nb (full lines) along the (001) direction in the Brillouin zone using the linear-response method described in the paper. Results of total-energy supercell calculations (circles) using the full-potential LMTO method [15] as well as experiment [17] (triangles). L, longitudinal; T, transverse modes.

linear-response theory excellently reproduces the overall features: (i) the correct long-wavelength behavior which shows that the acoustic sum rule is exactly satisfied; (ii) the dip in the longitudinal branch near the point $(2\pi/a)(0,0,0.7)$ which agrees with experiment within 0.06 THz; and (iii) softening of the transverse modes at long wavelengths. The elastic constants C_{11} and C_{44} estimated from the calculated sound velocities are within 2.6% of their measured values. All theoretical phonon frequencies agree remarkably well with experiment; the average discrepancy is only 0.9% and the maximum error is equal to 3.4%.

In conclusion, I have devised an *ab initio* linear-response method which does not rely on the pseudopotential approximation but on the muffin-tin basis sets. Application to the phonon dispersions in bcc Nb using linear-muffin-tin orbitals demonstrates that the method is fast and accurate.

The author is indebted to Professor O. K. Andersen for many helpful discussions. The support of the Max-Planck-Gesellschaft is gratefully acknowledged.

[a]On leave from P. N. Lebedev Physical Institute of the Russian Academy of Sciences, 117924 Moscow, Russia.

[1] For a review, see, e.g., *Theory of the Inhomogeneous Electron Gas,* edited by S. Lundqvist and S. H. March (Plenum, New York, 1983).

[2] K. Kunc and E. Tosatti, Phys. Rev. B **29**, 7045 (1984); A. Fleszar and R. Resta, Phys. Rev. B **31**, 5305 (1985); M. S. Hybertsen and S. G. Louie, Phys. Rev. B **35**, 5585 (1987).

[3] R. Resta and K. Kunc, Phys. Rev. B **34**, 7146 (1986); M. S. Hybertsen and S. G. Louie, Phys. Rev. B **35**, 5602 (1987).

[4] N. E. Zein, Fiz. Tverd. Tela (Leningrad) **26**, 3024 (1984) [Sov. Phys. Solid State **26**, 1825 (1984)]; S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987).

[5] S. Baroni, S. Gironcoli, and P. Giannozzi, Phys. Rev. Lett. **65**, 84 (1990); S. Baroni, P. Giannozzi, and E. Molinari, Phys. Rev. B **41**, 3870 (1990); R. D. King-Smith and R. J. Needs, J. Phys. Condens. Matter **2**, 3431 (1990); P. Giannozzi, S. Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B **43**, 7231 (1991); D. Kh. Blat, N. E. Zein, and V. I. Zinenko, J. Phys. Condens. Matter **3**, 5515 (1991); X. Gonze, D. C. Allan, and M. P. Teter, Phys. Rev. Lett. **68**, 3603 (1992).

[6] S. Yu. Savrasov, Solid State Commun. **74**, 69 (1990).

[7] N. E. Zein, Phys. Lett. A **161**, 526 (1992).

[8] R. M. Sternheimer, Phys. Rev. **96**, 951 (1954); **107**, 1565 (1957); **115**, 1198 (1959).

[9] For a review of frozen-phonon and perturbative methods, see, e.g., *Ab Initio Calculations of Phonon Spectra,* edited by J. T. Devreese, V. E. Van Doren, and P. E. Van Camp (Plenum, New York, 1983).

[10] Here, we do not mean *ab initio* calculations of single phonon modes by means of frozen-phonon techniques; we should also mention that many realistic calculations have been performed using the Varma-Weber method [C. M. Varma and W. Weber, Phys. Rev. Lett. **39**, 1094 (1977)], which is not completely *ab initio*; for a review of model calculations see, e.g., S. K. Sinha, in *Dynamical Properties of Solids,* edited by A. A. Maradudin and G. K. Horton (North-Holland, Amsterdam, 1980), Vol. 3.

[11] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[12] Some comments should be made on the notations used throughout the paper: $\delta^{\pm}$ produces the variation of a Bloch wave, whereby $\pm\mathbf{q}$ get added to its wave vector, e.g., $|\delta^{\pm}\mathbf{k}\lambda\rangle$ has the wave vector $\mathbf{k}\pm\mathbf{q}$ and $\delta^{\pm}\delta^{\mp}V_{\text{ext}}$ has wave vector $\mathbf{0}$. In (2), $|\delta^{\pm}\delta^{\mp}\mathbf{k}\lambda\rangle$ has the wave vector $\mathbf{k}$ and only these functions give nonzero contributions in the matrix elements with $|\mathbf{k}\lambda\rangle$.

[13] P. Pulay, J. Mol. Phys. **17**, 197 (1969).

[14] Note that in the KKR and augmented-plane-wave (APW) methods, the states $|\mathbf{k}\pm\mathbf{q}\lambda'\rangle$ in (6) will have the following meaning: Since the KKR (APW) energy bands $E_{\mathbf{k}\lambda}$ and eigenvectors $A_{\alpha}^{\mathbf{k}\lambda}$ are the eigenvalues and eigenvectors of the LMTO (LAPW) Hamiltonian $\langle\chi_{\beta}^{\mathbf{k}}(E_v)|H|\chi_{\alpha}^{\mathbf{k}}(E_v)\rangle$ with $E_v\equiv E_{\mathbf{k}\lambda}$, the states $|\mathbf{k}\pm\mathbf{q}\lambda'\rangle$ in (6) will be the eigenstates of $\langle\chi_{\beta}^{\mathbf{k}\pm\mathbf{q}}(E_{\mathbf{k}\lambda})|H|\chi_{\alpha}^{\mathbf{k}\pm\mathbf{q}}(E_{\mathbf{k}\lambda})\rangle$ and only those bands $E_{\mathbf{k}\pm\mathbf{q}\lambda'}$ with energy near $E_{\mathbf{k}\lambda}$ will be described correctly. In this case, finding $|\delta^{\pm}\mathbf{k}\lambda\rangle$ requires the knowledge of this auxiliary spectrum for *every* occupied energy $E_{\mathbf{k}\lambda}$.

[15] S. Yu. Savrasov and D. Yu. Savrasov, Phys. Rev. B (to be published).

[16] O. Jepsen and O. K. Andersen, Phys. Rev. B **29**, 5965 (1984).

[17] *Landolt-Börnstein, New Series, III/13a* (Springer-Verlag, Berlin, Heidelberg, New York, 1981).