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Ab initio calculation of phonon dispersions in II-VI semiconductors

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The vibrational properties of ZnSe, ZnTe, CdSe, and CdTe are determined by density-functional perturbation theory. To this end we have generalized this method so as to explicitly account for the nonlinear core correction to the exchange and correlation energy of systems treated with pseudopotentials. Furthermore, we have implemented a method to enhance the transferability of pseudopotentials of group-II atoms with shallow d electrons frozen in the core. The accuracy obtained in this way is similar to that previously achieved for elemental and III-V semiconductors.

Much attention is presently being paid to II-VI semiconductors and their alloys, especially because of their applicability to designing heterostructures which look very promising for optoelectronic applications in nonconventional frequency ranges.[1] Understanding the vibrational properties of these systems is important *per se* and for characterization purposes: this requires in turn an accurate knowledge of the bulk phonon dispersions of pure materials.

Density-functional theory (DFT) within the local-density approximation (LDA) has been shown to be able to describe very accurately the structural and lattice-dynamical properties of covalently bonded materials using pseudopotentials and plane-wave basis sets.[2] In the framework of density-functional perturbation theory (DFPT),[3,4] it has been possible to calculate phonon frequencies, dielectric constants, piezoelectric constants, effective charges, and other properties of elemental and III-V semiconductors with an accuracy of a few percent.[4,5]

The extension of these methods to II-VI semiconductors is not straightforward, the most serious problem being the presence of cation d electrons with energies of the order of 10 eV below the cation s electrons. The d electrons form a flat band whose energy is *higher* than the anion s band, and therefore they should be considered as valence electrons rather than frozen in the core: all-electron calculations[6] have indeed shown important contributions to bond formation by these electrons. The inclusion of localized d electrons in the valence shell is a major problem within the usual plane-wave (PW) formalism, because their wave functions cannot be expanded in a PW basis set of any reasonable size.

Two main reasons prevent shallow d electrons in II-VI materials from being straightforwardly frozen in the core: (i) Their spatial extension is large enough to determine a sizeable overlap with valence s electrons, thus making the linearization of the exchange-correlation (XC) energy with respect to the valence (s) and core (d) contribution questionable. (ii) Their small binding energy makes their wave functions dependent on the chemical environment, thus invalidating the frozen-core approximation which seems to underlie the pseudopotential method. A remedy for the first problem has been suggested a few years ago by Louie, Froyen, and Cohen,[7] and it is currently known under the name of the nonlinear core correction (NLCC). The idea is to evaluate the XC energy using the *total*—rather than *valence*—charge density: this is achieved by adding the frozen-core charge to the self-consistent valence charge. As for the second problem, it is worth mentioning that the frozen-core ansatz is not strictly needed for the pseudopotential approximation to be valid.[8] As a matter of fact, the NLCC has been recently applied to II-VI semiconductors[9-11] with encouraging results.

A nontrivial feature of the NLCC must be pointed out. When adopting a pseudopotential approach, one divides the total energy of the system as a core energy, a valence energy, and a core-valence interaction energy: the latter term is precisely the one whose accuracy is improved within the NLCC. As for the core energy, one wants this term to be a constant independent of the geometry, having the meaning of the core energy of isolated ions: such a requirement is particularly important when evaluating forces (as it is done here) or stresses (as in Ref. 10). It is straightforward to realize that the core energy of a condensed system fulfills such a requirement only if the core charges do not overlap: this in fact occurs for the binary systems studied here, when the core charge of cations only are retained in the calculation, while ordinary norm-conserving pseudopotentials are used for the anions. This is nonetheless enough to correctly account for d-electron effects.

In this work we generalize DFPT to the case where atoms are treated by the NLCC: when atoms are displaced, the valence charge density responds in this case to both displacements of the pseudopotential and of the core charge. As an application, we calculate the phonon spectra of ZnTe, ZnSe, CdTe, and CdSe in the zinc-blende phase. In order to achieve an accuracy similar to that previously obtained for elemental and III-V compounds, it proved useful to generate the NLCC pseudopotentials according to a scheme which partially accounts for the relaxation of d electrons by using more than one atomic reference configuration.

The basic quantities in lattice dynamics are the harmonic force constants, i.e., the second derivatives of the crystal energy with respect to the displacement of atoms from their equilibrium positions: these derivatives are simply related to the linear response of the valence charge to the perturbation.[4] We show here how the scheme proposed in Ref. 4 to calculate the dynamical matrix at arbitrary wave vectors is generalized to the framework of the NLCC. We simplify the notations using local pseudopotentials, even if the calculations are actually performed using nonlocal pseudopotentials; the generalization of the following expressions to the nonlocal case is, however, straightforward. The starting point is an extension of the Hellmann-Feynman theorem[12] to the case where the XC energy depends explicitly—through the core charge—on the atomic positions $\mathbf{u}_s$. For the sake of simplicitly, let us limit ourselves to the LDA from now on; in this case Hellmann-Feynman theorem reads

$$\frac{\partial E_{\rm tot}}{\partial \mathbf{u}_s} = \frac{\partial E_{\rm ion}}{\partial \mathbf{u}_s} + \int \rho_v(\mathbf{r}) \frac{\partial V_{\rm ps}(\mathbf{r})}{\partial \mathbf{u}_s} d\mathbf{r} + \int \mu_{\rm XC}(\rho(\mathbf{r})) \frac{\partial \rho_c(\mathbf{r})}{\partial \mathbf{u}_s} d\mathbf{r}, \qquad (1)$$

where $E_{\rm ion}$ is the ionic electrostatic energy, $V_{\rm ps}$ is the bare ionic pseudopotential of the crystal, ρ_v, ρ_c, and ρ are the valence, core, and total charge densities respectively, and $\mu_{\rm XC}(\rho(\mathbf{r}))$ is the functional derivative of the XC energy with respect to the density which—within NLCC-LDA—is an ordinary function of the total (core plus valence) charge at point $\mathbf{r}$. The first two terms give the usual expression for the force acting on the atom s, while the third one is the NLCC contribution. Further differentiation of Eq. (1) with respect to atomic positions leads to the desired harmonic force constants:

TABLE I. Comparison between theoretical predictions and experiments for the lattice constant (a_0), bulk modulus (B_0), dielectric constant (ϵ_∞), effective charge Z^*, and zone-center transverse-optic frequency ($\omega_{\rm TO}$). "BHS" indicates calculations made with the pseudopotentials of Ref. 14 without any NLCC; "$\rm NLCC_1$" indicates calculations including the NLCC and single-configuration pseudopotentials; "$\rm NLCC_2$" is the same as "$\rm NLCC_1$," but with multiconfiguration pseudopotentials (see text). LAPW indicates all-electron data from Ref. 6. Theoretical data are obtained with a 16-Ry kinetic-energy cutoff.

		a_0 (a.u.)	B_0 (Kbar)	ϵ_∞	Z^*	$\omega_{\rm TO}$ ($\rm cm^{-1}$)
ZnSe	BHS	10.04	798	5.9	1.78	238
	NLCC	10.70	650	6.3	2.01	219
	Expt.	10.72[a]	625[a]	6.3[b]	2.03[c]	212[d]
ZnTe	BHS	10.46	713	7.7	1.54	228
	NLCC	11.47	520	7.7	1.95	188
	LAPW	11.44	521			
	Expt.	11.50[a]	509[a]	7.3[e]	2.00[c]	177[b]
CdSe	BHS	10.16	935	5.4	1.69	229
	$\rm NLCC_1$	11.43	636	6.2	2.14	197
	$\rm NLCC_2$	11.48	571	6.2	2.20	187
	Expt.	11.50[a]	550[a]	6.2[b]	2.30[c]	
CdTe	BHS	11.12	666	6.7	1.67	182
	$\rm NLCC_1$	12.14	499	7.0	2.08	161
	$\rm NLCC_2$	12.19	453	7.2	2.17	152
	LAPW	12.23	440			
	Expt.	12.24[a]	445[a]	7.1[f]	2.35[c]	141[f]

[a] Reference 6.
[b] Reference 19.
[c] Reference 21.
[d] Reference 22.
[e] Reference 16.
[f] Reference 17.

$$\Phi_{\mathrm{s,s'}}=\frac{\partial^2 E_{\mathrm{tot}}}{\partial\mathbf{u}_{\mathrm{s}}\partial\mathbf{u}_{\mathrm{s'}}}=\frac{\partial^2 E_{\mathrm{ions}}}{\partial\mathbf{u}_{\mathrm{s}}\partial\mathbf{u}_{\mathrm{s'}}}+\int\rho_v(\mathbf{r})\frac{\partial^2 V_{\mathrm{ps}}(\mathbf{r})}{\partial\mathbf{u}_{\mathrm{s}}\partial\mathbf{u}_{\mathrm{s'}}}d\mathbf{r}$$
$$+\int\frac{\partial\rho_v(\mathbf{r})}{\partial\mathbf{u}_{\mathrm{s'}}}\frac{\partial V_{\mathrm{bare}}(\mathbf{r})}{\partial\mathbf{u}_{\mathrm{s}}}d\mathbf{r}$$
$$+\int\mu'_{\mathrm{XC}}(\rho(\mathbf{r}))\frac{\partial\rho_c(\mathbf{r})}{\partial\mathbf{u}_{\mathrm{s}}}\frac{\partial\rho_c(\mathbf{r})}{\partial\mathbf{u}_{\mathrm{s'}}}d\mathbf{r}$$
$$+\int\mu_{\mathrm{XC}}(\rho(\mathbf{r}))\frac{\partial^2\rho_c(\mathbf{r})}{\partial\mathbf{u}_{\mathrm{s}}\partial\mathbf{u}_{\mathrm{s'}}}d\mathbf{r}, \tag{2}$$

where we have defined

$$\frac{\partial V_{\mathrm{bare}}(\mathbf{r})}{\partial\mathbf{u}_{\mathrm{s}}}=\frac{\partial V_{\mathrm{ps}}(\mathbf{r})}{\partial\mathbf{u}_{\mathrm{s}}}+\mu'_{\mathrm{XC}}(\rho(\mathbf{r}))\frac{\partial\rho_c(\mathbf{r})}{\partial\mathbf{u}_{\mathrm{s}}}, \tag{3}$$

and $\mu'_{\mathrm{XC}}(\rho)$ is the derivative of the XC potential with respect to the electron density.

From Eq. (2) it is evident that—even including the NLCC—only the linear variation of the valence charge density induced by an atomic displacement is required in order to evaluate the harmonic force constants $\Phi_{\mathrm{s,s'}}$. Whenever the core charge ρ_c is neglected, the force constants reduce to those of Ref. 4, while its contribution to Eq. (2) is twofold: (i) the explicit appearance of the last two terms which are absent in the original expression; and (ii) the modification of the bare perturbation inducing the valence density variation, as in Eq. (3). These two modifications can be easily implemented in the DFPT approach of Ref. 4.

Norm-conserving pseudopotentials have been generated using a scheme originally proposed by von Barth and Car.[13] In this scheme, the semilocal potentials are assumed to depend on a few parameters. The usual choice is

$$V_l(r)=-\frac{Z_v}{r}\mathrm{erf}(\sqrt{\alpha_c}r)+(a_l+b_l r^2)e^{-\alpha_l r^2}, \tag{4}$$

where Z_v is the valence charge of the atom. The parameters α_c, α_l, a_l, and b_l are then determined by minimizing the squared differences between valence orbital energies and radial wave functions (beyond some core radius r_c) resulting from a self-consistent all-electron calculation and a pseudopotential one, made using Eq. (4). If the NLCC is considered, the core charge is also fitted to an analytical expression of the form:

$$\rho_c(\mathbf{r})=(a_{\mathrm{cc}}+b_{\mathrm{cc}}r^2)e^{-\alpha_{\mathrm{cc}}r^2}, \tag{5}$$

and used consistently in the generation of the pseudopotential. The pseudopotentials so generated have been tested by calculating a few structural, dynamical, and dielectric properties of the four compounds studied in this work. The data reported in Table I show that the inclusion of the NLCC determines a dramatic improvement in the agreement between theory on one side and all-electron calculations and experiment on the other side, with respect to calculations made using pseudopotentials available in the literature[14] which do not include any effects from the NLCC. This improvement, however, is not sufficient to bring the quality of the calculation to the level of accuracy achieved by pseudopotential DFT-LDA calculations for elemental and III-V semiconductors. This is particularly so for Cd compounds for which the electronic structure of the outermost d shell depends more sensitively on the valence configuration, and pseudopotentials generated from a single configuration are expected to be less transferable. In order to improve the transferability of Cd pseudopotentials—while maintaining the d electrons frozen in the core—we have modified the von Barth–Car scheme described above: instead of minimizing the squared differences relative to a single configuration, we minimize the weighted sum of the squared differences relative to several configurations. Of course, the very fact that pseudopotentials generated for one configuration are not accurately transferable to other configurations implies that the quality of the results could depend somewhat on the choice of the configurations and weights. The intrinsic arbitrariness of these pseudopotentials is therefore wider than usual, and their value can only be assessed by comparing theoretical predictions with experiments. The electronic configurations used for pseudopotential generation in this work are: $s^2p^3d^1$ for Se and Te; $s^1p^0d^0$ for Zn; and $s^2(1)$, $s^1p^{0.5}(0.2)$, and $s^1p^0d^0(0.5)$ for Cd. In the latter case, the numbers in

TABLE II. Pseudopotentials generated and used in this work. For a definition of the symbols, see Eqs. (4) and (5).

		cc	α_c	$l=0$	$l=1$	$l=2$
Zn	α	0.6808	0.9458	0.9270	0.4563	0.5314
	a	0.0741		5.6826	1.1907	−0.0582
	b	0.0460		−2.1774	−0.2317	0.3442
Cd	α	0.4595	0.7491	0.8439	1.1656	0.6806
	a	0.0423		8.8803	13.543	0.2229
	b	0.0165		−3.2504	−3.8335	1.9983
Se	α		0.8734	1.3679	1.0738	0.9796
	a			10.3230	3.9141	−0.0030
	b			−6.7581	−2.0456	0.1652
Te	α		0.7510	1.1954	0.9454	1.0107
	a			14.0290	8.5579	−0.6370
	b			−5.8013	−2.6530	3.0227

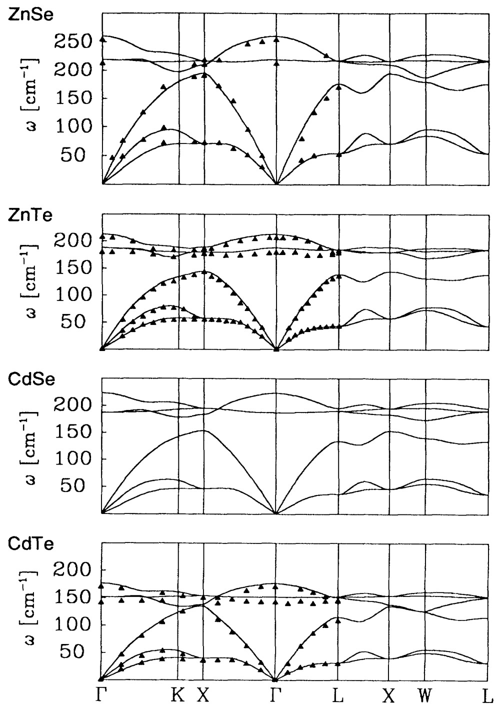

FIG. 1. Calculated phonon dispersions of ZnSe, ZnTe, CdSe, and CdTe. Triangles indicate experimental data from Refs. 22 (ZnSe), 16 (ZnTe), and 17 (CdTe).

parentheses are the weights of each configuration used, as explained above. The parameters of the resulting pseudopotentials are reported in Table II, together with the core charge parameters.

The theoretical NLCC-LDA phonon-dispersion relations of ZnSe, ZnTe, CdSe, and CdTe along several symmetry lines are shown in Fig. 1; these are compared to the neutron-diffraction data, wherever available. The agreement between the present calculations and the experimental data is of almost the same quality as previously obtained for elemental and group III-V semiconductors:[4] this gives us confidence in the reliability of the approximations used, in particular when low-symmetry crystal distortions are involved; the same level of accuracy (or order of 10 cm^{-1}) is expected from our predictions where the neutron data do not exist.

Our first-principles calculations, which are essentially parameter free, agree with experiments in a similar manner as previous semiempirical models depending on many adjustable parameters.[16,17,15] Some differences still exist, for instance concerning the TO branch of CdTe which is predicted to be flat in the present calculation, whereas it bends upwards according to the shell model of Ref. 17. In a recent paper[18] it has been suggested that the LO branch of ZnSe along some symmetry line should be rather flat, with a zone-edge frequency very close to the LO(Γ) frequency. Our calculations do not seem to support such a suggestion.

The case of CdSe deserves a special comment. In its most common form, it crystallizes in the wurtzite structure, whose parameters are almost ideally tetrahedral. The LO(Γ) frequency measured[19] on the wurtzite phase is 209–211 cm^{-1}, in good agreement with our theoretical zinc-blende-phase value of 222 cm^{-1}. Very recently, however, an experimental value of 201 cm^{-1} for the zinc-blende phase has been inferred from Raman-scattering measurements on superlattices.[20]

In this paper, we have shown how phonon dispersions of II-VI semiconductors can be obtained from first principles with essentially the same accuracy as in III-V and elemental semiconductors, and with virtually no further numerical effort. Neutron data are less informative for ZnSe and CdSe, where recent experiments of a different kind exist: our calculations show larger disagreements in this case, which we attribute to the rather indirect derivation of these data from superlattice or thin-layer measurements. A definite assessment of this issue, however, should require further experimental and theoretical investigations.

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