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Calculation of the first static hyperpolarizability tensor of three-dimensional periodic compounds with a local basis set: A comparison of LDA, PBE, PBE0, B3LYP, and HF results

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The computational scheme for the evaluation of the second-order electric susceptibility tensor in periodic systems, recently implemented in the CRYSTAL code within the coupled perturbed Hartree–Fock (HF) scheme, has been extended to local-density, gradient-corrected, and hybrid density functionals (coupled-perturbed Kohn–Sham) and applied to a set of cubic and hexagonal semiconductors. The method is based on the use of local basis sets and analytical calculation of derivatives. The high-frequency dielectric tensor (ϵ_∞) and second-harmonic generation susceptibility (d) have been calculated with hybrid functionals (PBE0 and B3LYP) and the HF approximation. Results are compared with the values of ϵ_∞ and d obtained from previous plane-wave local density approximation or generalized gradient approximation calculations and from experiment. The agreement is in general good, although comparison with experiment is affected by a certain degree of uncertainty implicit in the experimental techniques. © *2010 American Institute of Physics.* [doi:10.1063/1.3447387]

I. INTRODUCTION

The coupled perturbed Hartree–Fock (CPHF) method for computing nonlinear optical properties of solid-state systems has recently been implemented in a development version of the CRYSTAL program[1] within the periodic boundary conditions. Following Otto[2,3] and other authors,[4–8] we describe the effect of a static electric field ($\mathcal{E}^0$) applied to a crystal by inclusion of an additional perturbative term in the Hartree–Fock (HF) Hamiltonian of the form

$$\hat{\Omega}(\mathbf{k}) = \iota \mathcal{E}^0 \cdot e^{\iota \mathbf{k} \cdot \mathbf{r}} \nabla_\mathbf{k} e^{-\iota \mathbf{k} \cdot \mathbf{r}}, \tag{1}$$

with $\mathbf{r}$ and $\mathbf{k}$ representing any point in the real and the reciprocal space, respectively.

The total energy of the system can be expanded in a perturbative series of the field components (denoted by indices t, u, and v) starting from the total energy of the unperturbed system ($E_{\text{tot}}^{(0)}$),

$$E_{\text{tot}} = E_{\text{tot}}^{(0)} - \sum_t \mu_t \mathcal{E}_t^0 - \frac{1}{2} \sum_{t,u} \alpha_{tu} \mathcal{E}_t^0 \mathcal{E}_u^0$$
$$- \frac{1}{3!} \sum_{t,u,v} \beta_{tuv} \mathcal{E}_t^0 \mathcal{E}_u^0 \mathcal{E}_v^0 + \cdots. \tag{2}$$

All tensors of increasing rank in Eq. (2), such as the permanent electric dipole moment (μ), the polarizability (α), and the hyperpolarizability (β), can be computed by subsequent differentiation of E_{tot} with respect to the applied field components.

CPHF represents a suitable and efficient analytical method to evaluate the components of the tensors appearing in Eq. (2). The implementation of CPHF in CRYSTAL[9–12] is based on the equations proposed by Hurst and Dupuis[13] and adapted to the periodic boundary condition context.[4–6] All equations refer to a local basis set consisting of Gaussian-type atomic orbitals. The method is applicable to the calculation of linear and nonlinear optical properties of zero-, one-, two-, and three-dimensional systems with high accuracy and efficiency, even in the case of large unit cells.[10–12] This represents an important advancement in quantum *ab initio* modeling of electric field effects in materials, because all previous calculations reported in the literature, either based on the same method[7,8,14] or the modern theory of polarization,[15–17] concerned special cases such as polymers or small unit-cell three-dimensional crystals.

Preliminary HF calculations of the polarizability[10] and the first and second hyperpolarizabilities[12] on model systems, such as LiF with different periodicity (ideal LiF molecule, linear chain of LiF units, single layer, crystalline solid), demonstrated inner consistency and high numerical accuracy of our implementation of the method. Nevertheless, HF is known to generally undershoot the values of the (hyper)polarizability, particularly because of large overestimation of band gaps (the differences between energy eigenvalues are part of the perturbative formulas, as shown in Sec. II). For this reason, density functional theory (DFT) is generally recognized as a more appropriate choice in the calculation of dielectric properties of materials, with the exception of one-dimensional conjugated polymers,[18–20] as well as other delo-

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calized two-dimensional and three-dimensional systems, where conventional functionals are inadequate. In particular, we expect that hybrid functionals may produce results in better agreement with experiment than other pure DFT functionals because they reproduce band gaps more reliably in many cases. Indeed, the good performance of our implementation of the coupled-perturbed Kohn–Sham (CPKS) method for the calculation of the polarizability of crystalline solids has been shown in Ref. 21 for magnesium oxide, diamond, and silicon. Preliminary CPHF and CPKS calculations of the first hyperpolarizability have also been performed for urea molecular crystal and potassium dihydrogen phosphate.[22,23]

In the present paper, we present some formal aspects of our extension to the CPKS calculations of the first static hyperpolarizability tensor. We also analyze the importance of the main computational parameters involved in the calculation systematically, with reference to a set of semiconductors which has been investigated with different functionals. Results are compared with previous calculations and experimental data. All experimental data we refer to were obtained in the UV-visible range of the electric field or extrapolated to the static limit. Although comparability of static electric susceptibilities with data measured at finite frequency fields is not straightforward, it is expected not to be critical for this set of large, or relatively large, band-gap semiconductors. Also, phonon contributions to the polarizability and the second-harmonic generation (SHG) electric susceptibility, which are not taken into account in our calculations, can be considered negligible in this case.

The paper is organized as follows. In Sec. II we reconsider some steps of the computational scheme in order to show how the CPHF method has been extended to DFT. We also address long-range interaction terms in the Hamiltonian to which we referred collectively as two-electron integrals in Refs. 10 and 12, with no specification of the special treatment that makes periodic boundary calculations feasible and efficient. In Sec. III we first analyze the dependence of the achieved accuracy on the main computational parameters, such as basis set, choice of the DFT functional, and integration grid in reciprocal space. Then, we illustrate the results obtained from the calculation of the static polarizability and first hyperpolarizability for semiconductors having no inversion symmetry such as cubic SiC, BN, AlN, AlP, GaP, and hexagonal SiC and AlN.

II. THE METHOD

The components of the polarizability and first hyperpolarizability tensors for a periodic system in a local basis set can be calculated as second and third derivatives of the total energy [Eq. (2)] relative to the various components of the electric field.[4,5,10,13] A previous work[12] led us to the following expression for the polarizability α:

$$\alpha_{tu} = -\frac{2}{n_k}\Re\left(\hat{P}_{t,u}\sum_{\mathbf{k}}^{\text{BZ}}\sum_{j}^{\text{occ}}\sum_{l}^{\text{virt}}\Xi_{jl}^{(t)}U_{lj}^{(u)}\right), \qquad (3)$$

and to the $2n+1$ formulation for the first hyperpolarizability β:

$$\beta_{tuv} = -\frac{2}{n_k}\Re\left\{\hat{P}_{t,u,v}\sum_{\mathbf{k}}^{\text{BZ}}\sum_{j}^{\text{occ}}\sum_{l}^{\text{virt}}\left[U_{lj}^{(t)*}\left(\sum_{m}^{\text{virt}}G_{lm}^{(u)}U_{mj}^{(v)}\right.\right.\right.$$
$$\left.\left.\left.-\sum_{m}^{\text{occ}}U_{lm}^{(v)}G_{mj}^{(u)}+\imath\frac{\partial U_{lj}^{(v)}}{\partial k_u}\right)\right]+\beta_{tuv}^{\text{DFT}}\right\}, \qquad (4)$$

in the crystalline orbital (CO) basis set; all matrices depend on the $\mathbf{k}$ point; for brevity, however, these dependences have been omitted in the formulas.

In the above equations,

- n_k is the number of $\mathbf{k}$ points in the first Brillouin zone (BZ).

- $\Re$ is the real part of the expression in parentheses.

- $\hat{P}_{t,u,v}$ is the permutation operator of the t, u, and v field components.

- $\Xi_{ij}^{(t)}$ is the t component of $\hat{\Omega}(\mathbf{k})$ [Eq. (1)] in the unperturbed CO basis set developing on the atomic orbital (AO) $\varphi_\mu^{\mathbf{g}}$ located in the $\mathbf{g}$-cell,

$$\Xi_{ij}^{(t)} = \sum_{\mu\nu}^{\text{all}} C_{\mu i}^{(0)*}\Omega_{\mu\nu}^{(t)}C_{\nu j}^{(0)}. \qquad (5)$$

- $G_{ij}^{(u)}$ is the derivative of the Fock/Kohn–Sham matrix element between the ith and jth CO with respect to the u component of the applied electric field.

- $U_{ij}^{(v)}$ is a nondiagonal (occupied-virtual) element of the matrix describing the first derivative of the CO eigenvectors with respect to the field in the v direction,

$$C_j^{(v)} = \sum_j U_{ij}^{(v)}C_i^{(0)}, \qquad (6)$$

and such that

$$U_{ij}^{(v)} = \frac{G_{ij}^{(v)}}{E_j^{[0]} - E_i^{[0]}}, \qquad (7)$$

where $E_i^{[0]}$ is an eigenvalue of the ith unperturbed CO orbital.

- β_{tuv}^{DFT} appears in DFT approximations only and contains third-order derivatives of the exchange-correlation (XC) density functional (this term is discussed at the end of this section).

In CRYSTAL, the Fock matrix $\mathbf{F}$ is first calculated in the AO basis and then Fourier transformed to the CO basis, and so is its derivative with respect to the field. This latter depends not only on the field perturbation matrix $\Omega^{(t)}$ but also on the two-electron integrals multiplied by the first-order perturbation density matrix $D^{(t)}$,

$$D_{\mu\nu}^{\mathbf{g}(t)} = \sum_{\mathbf{k}} e^{\imath\mathbf{k}\cdot\mathbf{g}}\sum_i^{\text{occ}}(C_{\mu i}^{(t)}(\mathbf{k})^*C_{\nu i}^{(0)}(\mathbf{k}) + C_{\mu i}^{(0)}(\mathbf{k})^*C_{\nu i}^{(t)}(\mathbf{k})), \quad (8)$$

where $C^{(t)}$ is defined in Eq. (6).

We now examine the problem of the calculation of such derivatives in the case of a DFT calculation with a hybrid

functional, such as B3LYP. Other approximations, such as local density approximation (LDA), generalized gradient approximation (GGA), or HF, can be considered particular cases of that more general case. Hybrid functionals incorporate a fraction a_X of "exact" exchange and a complementary fraction of exchange functional of the density (f^X), which can be summed to the correlation part of the density functional (f^C) to give

$$f^{XC}(\rho, |\nabla \rho|^2) = (1 - a_X)f^X(\rho, |\nabla \rho|^2) + f^C(\rho, |\nabla \rho|^2). \quad (9)$$

For simplicity, we refer to a closed-shell system so that the functional depends on the total electron density ρ and the module squared of its gradient, $|\nabla \rho|^2$.

We focus on $\mathbf{F}^{e-e}$, the electron-electron repulsive interaction part of $\mathbf{F}$, as the other contributions to $\mathbf{F}$, i.e., the kinetic energy and electron-nuclear attraction integrals evaluated with reference to the AOs are not affected by the field (they contain no dependence on the density matrix)[10,11,13] and field derivatives are null. On the contrary, $\mathbf{F}^{e-e}$ depends explicitly on the density matrix and, according to Eq. (7), the change of the system operated by the perturbing field is contained in the derivatives of the density matrix. $\mathbf{F}^{e-e}$ in CRYSTAL, with the choice of a hybrid-functional DFT approximation, would include the following terms:

$$\mathbf{F}^{e-e} = \mathbf{F}^C_{sr} + \mathbf{F}^C_{wo} + \mathbf{F}^C_{lr} + a_X(\mathbf{F}^X_{sr} + \mathbf{F}^X_{wo}) + \mathbf{F}^{XC}_{DFT}. \quad (10)$$

Coulomb interactions between every electron in the reference unit cell and all the electrons of the infinite system are evaluated at different levels of approximation, depending on the kind of mutual interaction, i.e., short-range interactions ($\mathbf{F}^C_{sr}$), weakly overlapping electron distributions within a defined quantum radius ($\mathbf{F}^C_{sr}$), and long-range interactions ($\mathbf{F}^C_{wo}$). Similarly, exchange contributions are subdivided into short-range ($\mathbf{F}^X_{sr}$) and weakly overlapping interactions ($\mathbf{F}^X_{wo}$). The rest comes from the XC functional of the electron density and its gradient.

We now consider all terms in Eq. (10) for one general element of the $\mathbf{F}^{e-e}$ matrix in more detail.

(a)   Only interactions between overlapping electron distributions are evaluated as actual two-electron Coulomb integrals,

$$[F^C_{sr}]^{\mathbf{g}}_{\mu\nu} = \sum_{\rho,\tau} \sum_{\mathbf{g}'}^{\infty} D^{\mathbf{g}'}_{\rho\tau} \sum_{\mathbf{g}''}^{\infty} (\varphi^0_\mu \varphi^{\mathbf{g}}_\nu | \varphi^{\mathbf{g}''}_\rho \varphi^{\mathbf{g}'+\mathbf{g}''}_\tau). \quad (11)$$

(b)   Integrals relative to weakly overlapping electron distributions within the so-called "quantum zone"[24,25] are evaluated through multipolar expansions, $\gamma^m_\ell(\mu\nu\mathbf{g})$ and $\gamma^{m'}_{\ell'}(\rho\tau\mathbf{g}')$, of the two-electron distributions at their respective centroids coupled by potential terms ($V^{mm'}_{\ell\ell'}$) with the same quantum numbers ℓ, ℓ', m, and m',

$$[F^C_{wo}]^{\mathbf{g}}_{\mu\nu} = \sum_{\ell,m,\ell',m'} \gamma^m_\ell(\mu\nu\mathbf{g})$$
$$\times \sum_{\rho,\tau} \sum_{\mathbf{g}'} V^{mm'}_{\ell\ell'}(\mu\nu\rho\tau\mathbf{g}\mathbf{g}')D^{\mathbf{g}'}_{\rho\tau}\gamma^{m'}_{\ell'}(\rho\tau\mathbf{g}'), \quad (12)$$

the sum over $\mathbf{g}''$ lattice vectors being included in $V^{mm'}_{\ell\ell'}$.

(c)   Out of the "quantum zone," Coulomb contributions to $\mathbf{F}$ are computed as multipolar expansions of the interaction of every AO pair with the electron potential generated by the sublattice of every atom A in the unit cell, $\Phi^m_\ell(\mu\nu\mathbf{g}, A)$, saturated by $\Gamma^m_\ell(A)$, the corresponding atomic multipole moments,[25]

$$[F^C_{lr}]^{\mathbf{g}}_{\mu\nu} = \sum_A \sum_{\ell,m} \Gamma^m_\ell(A)\Phi^m_\ell(\mu\nu\mathbf{g}, A). \quad (13)$$

Only $\Gamma^m_\ell(A)$ multipoles contain an explicit dependence on the density matrix

$$\Gamma^m_\ell(A) = \sum_{\mu \in A} \sum_{\nu,\mathbf{g}'} D^{\mathbf{g}'}_{\mu\nu}\gamma^m_\ell(\mu\nu\mathbf{g}'). \quad (14)$$

(d)   As for the Coulomb part, only exchange integrals involving overlapping electron distributions are computed exactly,

$$[F^X_{sr}]^{\mathbf{g}}_{\mu\nu} = -\frac{1}{2}\sum_{\rho\tau} \sum_{\mathbf{g}'}^{\infty} D^{\mathbf{g}'}_{\rho\tau} \sum_{\mathbf{g}''}^{\infty} (\varphi^0_\mu \varphi^{\mathbf{g}''}_\rho | \varphi^{\mathbf{g}}_\nu \varphi^{\mathbf{g}'+\mathbf{g}''}_\tau). \quad (15)$$

(e)   Exchange integrals involving weakly overlapping electron distributions are approximated by coupling multipolar expansions like in case (b) [Eq. (12)],

$$[F^X_{wo}]^{\mathbf{g}}_{\mu\nu} = -\frac{1}{2}\sum_{\ell,m} \sum_{\rho} \sum_{\mathbf{g}'} \gamma^m_\ell(\mu\rho\mathbf{g}')\sum_{\tau} D^{\mathbf{g}'}_{\rho\tau}$$
$$\times \sum_{\ell',m'} \sum_{\mathbf{g}''} V^{mm'}_{\ell\ell'}(\mu\rho\nu\tau\mathbf{g}\mathbf{g}'\mathbf{g}'')\gamma^{m'}_{\ell'}(\nu\tau\mathbf{g}\mathbf{g}'\mathbf{g}''). \quad (16)$$

(f)   Following Pople et al.,[26] the DFT XC part of the Fock matrix is calculated by the following formula:

$$\mathbf{F}^{XC}_{DFT} = \sum_i w_i \left[\frac{\partial f^{XC}}{\partial \rho}\varphi^0_\mu \varphi^{\mathbf{g}}_\nu + 2\frac{\partial f^{XC}}{\partial |\nabla \rho|^2} \nabla \rho \cdot \nabla(\varphi^0_\mu \varphi^{\mathbf{g}}_\nu) \right]_{\mathbf{r}_i}. \quad (17)$$

The contributions in Eq. (17) are evaluated at points $\mathbf{r}_i$ of a grid and summed (numerical integration). Each grid point is associated with a geometrical weight w_i according to an atomic partition.[27] An efficient computational scheme for the implementation of Eq. (17) was proposed by Treutler and Ahlrichs.[28]

For all terms in Eq. (10), except $\mathbf{F}^{XC}_{DFT}$, the derivatives with respect to the components of the applied field are obtained simply by replacing the density matrix elements in Eqs. (11)–(16) with the corresponding density matrix elements derived by the field. The DFT-XC part depends on the density matrix elements through the electron density, which is expressed at each point $\mathbf{r}_i$ as

$$\rho(\mathbf{r}_i) = \sum_{\mu,\nu} \sum_{\mathbf{g}} D^{\mathbf{g}}_{\mu\nu}\varphi^0_\mu(\mathbf{r}_i)\varphi^{\mathbf{g}}_\nu(\mathbf{r}_i), \quad (18)$$

where the sums extend to all atomic orbitals contributing to the electron density at $\mathbf{r}_i$. Also in this case, the derivative of the density with respect to the tth component of the applied field (ρ^t) is obtained simply by replacing all $D^{\mathbf{g}}_{\mu\nu}$ elements

with $D_{\mu\nu}^{\mathbf{g}\,t}$ in Eq. (18). The same rule holds for the field derivative of the density gradient ($\nabla \rho^t$), because the two differentiation variables are independent of each other. However, the full derivative of Eq. (17) is complicated by the dependence of the functional on the density[29]

$$[\mathbf{F}_{\text{DFT}}^{XC}]_{\mu\nu}^{\mathbf{g}t} = \sum_i w_i \left\{ \left[\frac{\partial^2 f^{XC}}{\partial \rho^2} \rho^t + 2 \frac{\partial^2 f^{XC}}{\partial \rho\, \partial |\nabla \rho|^2} \nabla \rho \cdot \nabla \rho^t \right] \varphi_\mu^0 \varphi_\nu^{\mathbf{g}} \right.$$
$$+ 2 \left[\frac{\partial^2 f^{XC}}{\partial \rho\, \partial |\nabla \rho|^2} \rho^t + 2 \frac{\partial^2 f^{XC}}{\partial (|\nabla \rho|^2)^2} \nabla \rho \cdot \nabla \rho^t \right]$$
$$\left. \times \nabla \rho \cdot \nabla (\varphi_\mu^0 \varphi_\nu^{\mathbf{g}}) + 2 \frac{\partial f^{XC}}{\partial |\nabla \rho|^2} \nabla \rho^t \cdot \nabla (\varphi_\mu^0 \varphi_\nu^{\mathbf{g}}) \right\}_{\mathbf{r}_i}. \tag{19}$$

Weights w_i are purely geometric entities and do not depend on the applied field, nor do the atomic orbitals.

At variance with Eq. (17), second-order derivatives of the XC density functional appear in Eq. (19). In the calculation of β [Eq. (4)], the β^{DFT} term also contains third-order derivatives of the XC density functional,

$$\beta_{tuv}^{\text{DFT}} = \sum_i w_i \left[\frac{\partial^3 f^{XC}}{\partial \rho^3} \rho^t \rho^u \rho^v + 2 \frac{\partial^3 f^{XC}}{\partial \rho^2\, \partial |\nabla \rho|^2} \right.$$
$$\times \hat{P}_{t,u,v}(\rho^t \rho^u \nabla \rho \cdot \nabla \rho^v) + 4 \frac{\partial^3 f^{XC}}{\partial \rho\, \partial (|\nabla \rho|^2)^2}$$
$$\times \hat{P}_{t,u,v}(\rho^t \nabla \rho \cdot \nabla \rho^u \nabla \rho \cdot \nabla \rho^v)$$
$$+ 8 \frac{\partial^3 f^{XC}}{\partial (|\nabla \rho|^2)^3} \nabla \rho \cdot \nabla \rho^t \nabla \rho \cdot \nabla \rho^u \nabla \rho \cdot \nabla \rho^v$$
$$+ 2 \frac{\partial^2 f^{XC}}{\partial \rho\, \partial |\nabla \rho|^2} \hat{P}_{t,u,v}(\rho^t \nabla \rho^u \cdot \nabla \rho^v)$$
$$\left. + 4 \frac{\partial^2 f^{XC}}{\partial (|\nabla \rho|^2)^2} \hat{P}_{t,u,v}(\nabla \rho \cdot \nabla \rho^t \nabla \rho^u \cdot \nabla \rho^v) \right]_{\mathbf{r}_i}. \tag{20}$$

These XC functional derivatives are calculated using the XC-FUN library written by Ekström[30,31] for arbitrary-order XC functional derivatives using automatic differentiation, which has been interfaced to the CRYSTAL program.

III. RESULTS AND DISCUSSION

With the extension of our CPHF implementation to DFT (CPKS) we are in a position to assess reliability and accuracy of *ab initio* single-determinantal approximations in the calculation of optical properties of materials. In particular, we consider how the choice of Hamiltonian, basis set, and computational parameters influences the determination of the static dielectric tensor and first nonlinear electric susceptibility. In a three-dimensional crystal, the dielectric tensor components are proportional to the corresponding components of the polarizability tensor [Eq. (3)] through the following relation:

$$\epsilon_{tu} = \delta_{tu} + 4\pi V^{-1} \alpha_{tu}, \tag{21}$$

with V denoting the unit cell volume, and the first nonlinear electric susceptibility components are proportional to the first hyperpolarizability [Eq. (4)],

$$\chi_{tuv}^{(2)} = 2\pi V^{-1} \beta_{tuv}. \tag{22}$$

Therefore, ϵ and $\chi^{(2)}$ depend on the derivatives of the density matrix and the perturbative matrices $\mathbf{\Omega}$, as stated in Eqs. (3) and (4). Both the density matrix derivatives and $\mathbf{\Omega}$ are strongly affected by the system band structure, as differences of unperturbed CO energies appear in their definition.[10] For example, differences between occupied and virtual orbital energies appear in the denominator of Eq. (7) to define the matrix $\mathbf{U}^{(t)}$ which operates a unitary transformation of the unperturbed to the perturbed eigenvectors, in terms of which the $\mathbf{D}^{(t)}$ matrices are expressed [Eqs. (6)–(8)]. It is then to be expected that well determined band gaps are crucial for the accurate calculation of the ϵ and $\chi^{(2)}$ tensors, particularly in the case of compounds with small band gaps, where the denominator in Eq. (7) may be correspondingly small and large $\mathbf{U}^{(t)}$ matrix elements are to be expected. On the other hand, it is well known that band gap widths predicted by *ab initio* calculations vary considerably with the various Hamiltonians. LDA, for example, is known to largely underestimate band gaps, whereas HF generally overestimates them, even by a factor of 2 or more, so that some insulators are predicted to be metallic by LDA, whereas their insulating properties are overemphasized by HF. Consequently, HF is expected to produce low values for the electric susceptibility tensor components and LDA large values.

The dielectric tensor ϵ is diagonal in all cases here considered and all its components are equivalent by symmetry in cubic SiC, BN, AlN, AlP, and GaP (zinc-blende structure), whereas there are two nonequivalent components ($\epsilon_{xx} = \epsilon_{yy}$ and ϵ_{zz}) in hexagonal SiC and AlN (wurtzite structure). Similarly, there exists only one non-null component of $\chi^{(2)}$, i.e., $\chi_{xyz}^{(2)}$, for the cubic systems and two, $\chi_{xxz}^{(2)}$ and $\chi_{zzz}^{(2)}$, in the case of the hexagonal systems.

The influence of the parameters controlling the calculation of the dielectric ϵ and the SHG electric susceptibility $d = (1/2)\chi^{(2)}$ tensors has been analyzed for cubic SiC (d depends only on the electronic contribution at high frequencies such as ϵ_∞). Most of these parameters also determine the accuracy of the calculated properties of the unperturbed system and their effect is known. However, how far they affect ϵ and d still needs to be checked. In particular, we examined the dependence of the results on the basis set, the truncation of the Coulomb and exchange series, the kind of grid used to integrate the XC density functional, the density of the Monkhorst net for integrations in the reciprocal space, the convergence level of the SCF cycle, as well as the convergence level of the coupled-perturbed cycle.

Convergence of the SCF cycle is evaluated by T_E, a parameter measuring the total energy difference ΔE_{tot} (in hartree) between two subsequent cycles: the SCF procedure stops when $\Delta E_{\text{tot}} < 10^{-T_E}$. As transformations from the AO to the CO basis and vice versa are intrinsic in our implementation of the coupled-perturbed method, T_E needs to be large

TABLE I. Dependence of the dielectric constant ϵ and the second-harmonic generation electric susceptibility $d=(1/2)\chi^{(2)}_{xyz}$ (in pm/V) of cubic silicon carbide on the Monkhorst net shrinking factor S. All calculations were performed at the experimental lattice parameter ($a_{exp}=4.358$ Å) with the B3LYP functional and the 8-41(d)G (Si) and 6-21(d)G (C) basis sets.

S	ϵ	d
8	5.9458	12.2054
10	5.9030	12.1096
12	5.8948	12.0903
14	5.8932	12.0862
16	5.8929	12.0854
18	5.8929	12.0853

TABLE II. Effect of the computational parameter T_I controlling the truncation of the Coulomb and exact exchange (B3LYP only) series on ϵ and d for cubic SiC with the B3LYP and PBE approximations. The higher the T_I, the more accurate the selection of the integrals to be calculated (for further details see text and Ref. 32). Other conditions and units are as in Table I.

	B3LYP		PBE	
T_I	ϵ	d	ϵ	d
6	5.8924	12.0141	6.5985	16.9359
7	5.8970	12.0559	6.6007	16.9594
8	5.8948	12.0903	6.6004	16.9714
10	5.9028	12.1204	6.6004	16.9618
12	5.9071	12.1814	6.6005	16.9666
14	5.9126	12.2412	6.6003	16.9651
16	5.9140	12.2567	6.6002	16.9682
18	5.9083	12.2351	6.6002	16.9653
20	5.9150	12.2669	6.6002	16.9651

enough that sufficient accuracy in the determination of the eigenvectors for the unperturbed system is guaranteed. In the case of SiC, the uncertainty in the determination of ϵ is found to be below 0.002% with $T_E=6$, the default value for a total-energy calculation,[32] and it is below 0.01% for d. This is beyond the general accuracy of experimental measurements for both ϵ and d. With $T_E=9$ also the value of d becomes accurate up to the fourth decimal digit, the error being below 0.001%. A similar parameter, T_{CP}, is used to evaluate convergence of the coupled-perturbed cycle based on the assessment of the accuracy of the polarizability α. Tests on SiC show that the same kind of accuracy obtained for ϵ is obtained also for d.

The importance of the definition of the Monkhorst net in the calculation of ϵ and d deserves some attention as the nets used for total energy calculations do not appear to be equally adequate in this case for small unit cell systems. This is documented in Table I. S is the shrinking factor used to generate the commensurate net of points at which the Fock matrix is diagonalized and the CPHF equations are integrated (the total number of points in the first Brillouin zone is S^3 with no symmetry). Table I shows that at the lowest reported level, $S=8$, the error with respect to the converged result is about 1% and it reduces to 0.01% at $S=14$.

Other important parameters for an accurate evaluation of ϵ and d are the thresholds used for the truncation of the Coulomb and exchange series, collectively denoted as T_I in Table II. T_I represents a set of five computational parameters identified as T1, T2, T3, T4, and T5 in the CRYSTAL manual.[32] Results in Table II were obtained with the following setting: T1=T2=T3=T4=T_I, T5=2T_I (default setting: T_I=6). The cost of the SCF calculations is mostly determined by the calculation of two-electron integrals, whose number is controlled by T_I, so that this is an important parameter to be kept under control. Data for two different functionals, B3LYP and PBE, are shown in Table II in order to allow for a comparison between a situation where only the Coulomb series are calculated (PBE) and that where also the exact-exchange series are involved (B3LYP). T_I appears to be the most delicate parameter in the evaluation of ϵ and, particularly, of d. The default value of T_I (T_I=6) adopted in the CRYSTAL code provides B3LYP results that differ from well converged values (T_I=20) by about 2%, worse than with PBE by one order of magnitude. At T_I=10, the B3LYP error decreases to about 1% (0.1% with PBE). More severe con-

ditions reduce the numerical error to less than 1%. In contrast, the definition of the DFT integration grid is not more critical in the evaluation of ϵ and d than for total energy calculations. A change from the predefined[32] "small" grid (55 radial points and 434 angular points) to the "XL" grid (75 radial points and 974 angular points) gives an improvement smaller than 0.1%.

Table III shows the importance of including polarization functions into a double-zeta basis set (8-41G for Si and 6-21G for C) for the calculation of ϵ and d. In particular, both ϵ and d vary monotonically when improving the basis set and their values change by at least two to three orders of magnitude more rapidly than E_{tot}; ϵ increases by about 7% between basis sets A and I and d decreases by nearly 18%, whereas the corresponding E_{tot} changes by less than 0.02%. d appears to be generally more responsive to basis set changes than ϵ because the description of higher-order atom polarizabilities requires the inclusion of higher angular-momentum orbitals. For example, augmenting basis set A with one d-type AO for Si (basis set B) improves the value of d only by approximately 1/4 with respect to the most accurate value reported in the table (basis set I), while having a negligible effect on ϵ and, on the other hand, a relatively strong impact on E_{tot}. As expected, addition of d-type AOs is

TABLE III. Dependence of ϵ and d of cubic SiC on the basis set. α_X (bohr^{-2}) denotes the exponents of the polarization AOs at atom X with the highest angular momentum. ΔE is the total energy difference (mHa) from the total energy obtained with basis set A (-327.5270 hatree). Units and other computational conditions are as in Table I.

	Si	C	α_{Si}	α_C	ΔE	ϵ	d
A	8-41	6-21	$\cdots$	$\cdots$	0	5.6999	12.7824
B	8-41(d)	6-21	0.55	$\cdots$	39.2	5.6821	12.2089
C	8-41(d)	6-21(d)	0.55	0.61	42.1	5.8948	12.0903
D	8-41(dd)	6-21(d)	2.12, 0.42	0.61	46.6	5.9819	11.7821
E	8-41(dd)	6-21(dd)	2.12, 0.42	1.3, 0.4	47.6	6.0476	11.2014
F	8-41(dd,f)	6-21(dd)	0.45	$\cdots$	53.4	6.0801	10.8073
G	8-41(dd,f)	6-21(dd,f)	0.45	0.5	54.5	6.0981	10.5535
H	8-41(dd,ff)	6-21(dd,f)	1.35, 0.45	0.5	54.8	6.0998	10.5529
I	8-41(dd,ff)	6-21(dd,ff)	1.35, 0.45	1.5, 0.5	54.8	6.1035	10.5064

TABLE IV. Dielectric constant (ϵ) and SHG electric susceptibility ($d = (1/2)\chi^{(2)}$) of cubic SiC obtained with different methods. The results from the present work (rows 1–5) were obtained with basis set I in Table III at the experimental lattice parameters: 4.358 Å. d is in pm/V and the gap is in eV.

Method	ϵ	d	Gap
LDA	6.85	15.0	6.32
PBE	6.85	14.8	6.26
B3LYP	6.10	10.5	8.02
PBE0	6.19	10.5	8.28
HF	5.05	5.54	15.3
PW-LDA		12.4[a]	
+scissors		8.00[a]	
PW-LDA		8.83[b]	
PW-LDA-GW		7.45[b]	
+scissors		5.71[b]	
Experiment	6.52[c]	6.2–8.7[d]	6.0[e]
	6.22[e]		

[a]Reference 33.
[b]Reference 34.
[c]Reference 40.
[d]Reference 35 ($\lambda = 1064$ nm).
[e]Reference 41.

more important than further addition of f-type AOs. However, whereas f-type AOs account only for 1% improvement in the value of ϵ (upon an overall 7% change), they contribute almost 1/3 of the correction to d from basis set improvements, the inclusion of a second set of f-type polarization functions being less important.

We can now compare results obtained from different definitions of the Hamiltonian. We use the experimental geometry, $S=12$, $T_E=10$, $T_I=8$ (tighter tolerances need to be used in order to evaluate the exchange series within the HF calculations in order to achieve good SCF convergence; in particular, ITOL4 and ITOL5 (Ref. 32) were set to 14 and 28, respectively) and basis set I in Table III for SiC.

The values of ϵ and d predicted for cubic SiC with the different forms of the Hamiltonian (Table IV) appear to be closely related to the predicted gap width. Smaller gaps, as determined within the LDA and GGA approximations, correspond to higher values of ϵ and d, whereas low values of ϵ and d are obtained with HF, which is known to overestimate band gaps dramatically. Correspondingly, intermediate estimates are obtained with the hybrid functionals B3LYP and PBE0, which are known to approximate band gap widths fairly well in most cases. Such a trend for ϵ is to be expected, because the gap appears in transition energies in the denominator of the **U**-matrix [Eq. (7)] so that the larger the gap, the smaller the perturbation and response property, and vice versa. The same trend is shown by d in this case, but the interpretation is less straightforward, because d includes both positive and negative transition terms, whose balance is not easily predictable.

We compare these results with those obtained from previous calculations by different methods and data from experimental measurements. The LDA value of d for cubic SiC reported in Ref. 33 is reasonably close to the LDA result reported in this work. The value calculated by Adolph *et al.*[34] is, instead, lower than the other calculated results, in spite of

the same kind of approximations being used. The reason for this discrepancy may be associated with the use of a numerical basis set. Hybrid functionals generally decrease the values of d, not only as a consequence of increasing the gap with respect to LDA, but also because of the change in matrices **U** and **G** in Eq. (4). In this respect, this is a more genuine and consistent effect than application of the scissors operator[33] or inclusion of the GW correction,[34] which only affects the gap. Experimental values are reported in the equivalent hexagonal crystallographic system and the values reported in Table IV were transformed by the following identities: $d_{xyz}=(\sqrt{3}/2)d_{zzz}=-\sqrt{3}d_{xxz}$. Only few experimental data are available. In particular, Lundquist *et al.*[35] measured d on a polycrystalline β-BIC film and even the relation $d_{zzz}/d_{xxz}=-2$, which should hold for cubic systems, is far from being verified ($d_{zzz}/d_{xxz}=-2.8$) and the values obtained from transformation of both d_{xxz} and d_{zzz} to d_{xyz} are reported in Table IV. Therefore, the comparison between calculated and experimental results is affected by this kind of uncertainty.

SiC also exists under about a hundred different polytypes, thus offering the possibility of analyzing how the crystalline structure affects the SHG susceptibility.[34] For this reason it has been the object of careful investigation. Among these various polytypes we considered two different hexagonal phases, 2H–SiC and 6H–SiC, possessing anisotropic ϵ and d tensors (Table V). The consequent deviation of the d_{zzz}/d_{xxz} ratio from -2 is remarkable for 2H–SiC, ranging between -1.29 (HF) and -0.84 (PBE0). Chen *et al.*[33] and Adolph *et al.*[34] report an even larger deviation from the isotropic limit for the d_{zzz}/d_{xxz} ratio, ranging from -0.62 to -0.71, whereas our corresponding LDA value is -0.93. Unfortunately, no experimental data are available for comparison in this case.

The d tensor is much less anisotropic in 6H–SiC. The deviation of the d_{zzz}/d_{xxz} ratio from the isotropic limit is largest (-1.84) in the HF approximation and smallest (-2.02) with LDA. Aulbur *et al.*,[36] Chen *et al.*,[33] and Adolph *et al.*[34] report values ranging from -1.78 to -1.85. On the experimental side, Singh *et al.*[37] predict a ratio of -1.67 with an uncertainty of about ± 0.3. The other experimental data reported in Table V correspond to ratios as large as -6 or -10 and appear to be less reliable. Considering the actual values of ϵ and d, our LDA and PBE results best approximate the data reported in Ref. 37.

In Tables VI and VII the results for a series of III–V cubic semiconductors from the present work are compared with those from previous calculations and experimental measurements, when available. Basis sets of the same quality as I in Table III were used for B, Ga, N, and P atoms. Electric properties appear to be related to both the band structure and ion size, so that ϵ for AlP and GaP is about twice as large as for BN and AlN, whereas d for phosphides (d being very sensitive to cation-anion difference) is at least ten times as large as for nitrides. The band gap in BN (9–11 eV) is much larger than in the other cases, with GaP exhibiting the lowest gap (2.9 eV) and the direct influence of band gaps on the values of the polarizability through the matrix **U** has already been pointed out. It has also to be recalled that such a relation is less straightforward for d and this explains why d for

TABLE V. Dielectric (ϵ) and SHG electric susceptibility (d) tensor components of hexagonal 2H–SiC and 6H–SiC obtained with different methods at the experimental lattice parameters (3.079 and 5.053 Å for 2H–SiC and 3.081 and 15.125 Å for 6H–SiC). Computational conditions and units are as in Table IV.

	Method	ϵ_{xx}	ϵ_{zz}	d_{xxz}	d_{zzz}	Gap
2H–SiC	LDA	6.85	7.22	−7.70	7.13	4.65
	PBE	6.83	7.22	−7.63	6.57	4.69
	B3LYP	6.07	6.37	−5.78	5.66	6.29
	PBE0	6.16	6.48	−5.78	4.84	6.51
	HF	5.00	5.21	−3.19	4.10	12.9
	PW-LDA[a]			−6.6	4.7	
	+scissors[a]			−4.4	3.1	
	PW-LDA[b]			−3.55	2.25	
	PW-LDA-GW[b]			−1.95	1.25	
	+scissors[b]			−1.75	1.1	
6H–SiC	LDA	6.90	7.14	−9.06	18.3	5.04
	PBE	6.89	7.14	−8.94	17.6	5.08
	B3LYP	6.11	6.26	−6.15	11.8	6.69
	PBE0	6.20	6.36	−6.15	11.6	6.92
	HF	5.04	5.12	−3.22	5.89	13.4
	PW-LDA[c]	7.0	7.24	−7.5	13.8	6.95
	+scissors[c]	6.27	6.46	−5.2	9.3	
	PW-LDA[a]			−8.0	14.7	
	+scissors[a]			−5.5	10.0	
	PW-LDA[b]			−4.9	9.05	
	PW-LDA-GW[b]			−2.3	4.15	
	+scissors[b]			−2.55	4.55	
	Experiment	6.67[d]	6.88[d]	−9.8 ± 1[d]	16.4 ± 1.5[d]	4.3[e]
		6.52[f]	6.70[f]	−2 ± 1[g]	12 ± 0.5[g]	
				−2.5[h]	25[h]	

[a]Reference 33.
[b]Reference 34.
[c]Reference 36.
[d]Reference 37 ($\lambda = 1064$ nm).
[e]Reference 41.
[f]Reference 40.
[g]Reference 42 ($\lambda = 1064$ nm).
[h]Reference 35 ($\lambda = 1064$ nm).

TABLE VI. Dielectric constant (ϵ) and SHG electric susceptibility (d) of zinc-blende BN and AlN obtained with different methods and all-electron basis sets for all atoms [6-21(d) for B and N, 8-21(d) for Al]. The experimental lattice parameters (3.616 Å for BN, 4.318 Å for AlN) were used. Other computational conditions and units are as in Table IV.

	Method	ϵ	d	Gap
BN	LDA	4.63	2.97	8.75
	PBE	4.65	2.90	8.89
	B3LYP	4.37	2.46	10.9
	PBE0	4.42	2.39	11.3
	HF	3.95	1.82	19.3
	PW-LDA[a,b]	4.56	2.80	
	PW-LDA[c]		2.6	
	+scissors[c]		1.7	14.5
	LMTO-LDA[d]	4.14		
	Experiment[e]	4.5		8.2
AlN	LDA	4.57	0.0046	4.45
	PBE	4.58	0.18	4.42
	B3LYP	4.09	−0.12	6.30
	PBE0	4.18	0.16	6.41
	HF	3.42	0.03	13.5
	PW-LDA[a,c]	4.61	0.01	
	+scissors[c]		0.005	
	LMTO-LDA[d]	3.90		

[a]Reference 38.
[b]Reference 36.
[c]Reference 33.
[d]Reference 43.
[e]Reference 41.

small values. The agreement of results obtained with different methods is fairly good also in this case, particularly for the d_{zzz} component, which is not as small as d_{xxz}. However, comparison of calculated to experimental results is affected in this case by the uncertainty of the experimental measurements: ϵ is reported as "dielectric constant," with no distinction between anisotropic components, and the uncertainty on d_{zzz} extends to more than 50% of its values.

IV. CONCLUSIONS

The CPHF/CPKS method, recently implemented in the CRYSTAL program, has been applied to the calculation of the static dielectric and the second-order electric susceptibility tensors for a set of semiconductors, with the aim of assessing the general performance of the method as compared to other theoretical methods and experimental measurements. These calculations of $\chi^{(2)}$ of three-dimensional systems were performed with local basis sets and different approximations of the XC density functional, including hybrid functionals.

The present work establishes a protocol to obtain accurate estimates of the $\chi^{(2)}$ tensor components with respect to the choice of the basis set and appropriate computational conditions. In particular, availability of a well designed basis set, enriched with polarization functions with relatively high-order angular momentum, is more important in this case than for a standard SCF calculation. Use of a denser Pack–Monkhorst net and more severe T_I thresholds for the truncation of the Coulomb and exchange series ($T_I = 10$ instead of 6) is also important to improve the quality of results. If these conditions are met, the method is accurate and efficient.

AlN is in the same order of magnitude as for BN. At the same time, the growing size of ions associated with increasing unit cells, from a lattice parameter of 3.62 Å for BN to 5.45 Å for GaP, makes them increasingly more polarizable. The overall agreement of our LDA results with previous calculations at the same approximation level is good, particularly with the results reported in Refs. 33, 36, 38, and 39. The use of a basis set including d- and f-type polarization functions is very important for obtaining accurate values of d for all these systems. The d values obtained with basis sets of lower quality, like basis C in Table III, still have at least 50% error. Comparison among calculated results is more difficult in the case of GaP, because these are rather sparse, and the same sparsity is observed also in the experimental data available for d.

Experimental data are also available for AlN, which exists in the wurtzite structure and exhibits anisotropic behavior, as lattice parameters are 3.11 and 4.98 Å, respectively ($3.11\sqrt{3} = 5.39$). Results are reported in Table VIII. In contrast with SiC, the two independent components of d show the same sign and all methods and measurements predict

TABLE VII. Dielectric constant (ϵ) and SHG electric susceptibility (d) of zinc-blende AlP and GaP obtained with different methods and all-electron basis sets for all atoms [86-21(dd,ff) for Al, 86-4111(dd,ff) for Ga, 85-21(dd,ff) for P] at the experimental lattice parameter (5.421 Å for AlP and 5.448 Å for GaP). Other computational conditions and units are as in Table IV.

	Method	ϵ	d	Gap
AlP	LDA	8.02	23.2	3.60
	PBE	7.82	21.5	3.81
	B3LYP	6.79	15.3	5.15
	PBE0	6.86	14.9	5.45
	HF	5.35	7.62	11.3
	PW-LDA[a]	8.2	19.5	3.5
	PW-LDA[b,c]	8.3	23	
	+scissors[b,c]	7.2	15	3.63
	PW-LDA[d]		22.5	
	PW-GGA[d]		21	
	Experiment[e]	7.5		3.6
GaP	LDA	9.51	47.6	2.2
	PBE	9.13	42.4	2.4
	B3LYP	7.95	30.1	3.5
	PBE0	7.74	24.6	3.1
	HF	5.86	12.5	9.7
	PW-LDA[a]	9.8	34	2.8
	PW-LDA[b]	10.5	64.5	2.8
	PW-LDA[c]	10.4	60	
	+scissors[c]	8.8	35	
	PW-LDA[d]		65.5	
	PW-GGA[d]		57	
	Experiment	9.0[e]	35.5[f]	2.9
		9.4[g]	81.7[g]	
			41[h]	

[a]Reference 44.
[b]Reference 36.
[c]Reference 39.
[d]Reference 45.
[e]Reference 46 (static limit).
[f]Reference 47.
[g]Reference 48 (λ=1318 nm).
[h]Reference 49 (λ=632.8 nm).

TABLE VIII. Dielectric (ϵ) and SHG electric susceptibility (d) tensor components of the wurtzite AlN system obtained within different methods at the experimental lattice parameters: 3.11 and 4.98 Å. Computational conditions and units are as in Table VI. Experimental data for ϵ are reported as "dielectric constant" with no reference to any particular tensor component.

Method	ϵ_{xx}	ϵ_{zz}	d_{xxz}	d_{zzz}	Gap
LDA	4.49	4.79	0.43	4.33	4.02
PBE	4.49	4.80	0.37	4.50	4.00
B3LYP	4.04	4.26	0.39	2.71	5.82
PBE0	4.11	4.36	0.28	3.33	5.94
HF	3.40	3.53	0.19	1.24	13.1
PW-LDA	4.42[a,b]	4.70[a,b]	0.24[a]	4.61[a,b]	6.2[b]
PW-LDA[c]			0.1	4.2	
+scissors[c]			0.1	2.3	
FLAPW-LDA[d]	3.91	3.97	0.13	1.88	
LMTO-LDA[e]	3.91	3.77			
Experiment	4.68[f]	4.84[g]	$\leq |0.31|$[h]	7.8 ± 4.3[h]	5.9 ± 0.2[i]

[a]Reference 38.
[b]Reference 36.
[c]Reference 33.
[d]Reference 50.
[e]Reference 43.
[f]Reference 51.
[g]Reference 52 (λ=550 nm).
[h]Reference 53 (λ=1064 nm).
[i]Reference 54.

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Comparison with results obtained in previous calculations is only possible for the LDA approximation, with the exception of one GGA calculation for AlP and GaP.[45] Despite the difference in the basis set (Gaussian functions versus plane waves) and the method used to compute derivatives with respect to the electric field (fully analytical versus numerical), our CPKS calculations (LDA) are in generally good agreement with those reported in the literature. The agreement with experimental results is generally satisfactory. In many cases, however, such a comparison is affected by various sources of non-negligible errors, either associated with the experimental techniques or due to the sample features, such as for example a polycrystalline structure. Moreover, the dependence of the electric susceptibility on the field frequency should be accounted for in our calculation, particularly for the SHG process where the UV-visible resonances are reached twice as fast as in the dispersion of the high-frequency dielectric ϵ_∞ function. This will be the object of future work.

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