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Coupled Perturbed Kohn-Sham calculation of static polarizabilities of periodic compounds.

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Abstract. The Coupled Perturbed Hartree-Fock (CPHF) scheme recently implemented in the CRYSTAL06 code for systems periodic in 1-3 dimensions has been generalized to Density Functional Hamiltonians (CPKS, Coupled Perturbed Kohn-Sham). The dielectric tensor of Magnesium Oxide, Diamond, and Silicon is calculated with four different Hamiltonians, ranging from DFT, in the local density and gradient corrected approximations, to “hybrid” functional B3LYP and Hartree-Fock. The effect of the computational parameters (Pack-Monkhorst net and basis set) is explored. DFT is shown to perform generally better than HF, as it is the case for other properties such as band gaps (which influence the CPHF and CPKS equations via the energy difference between occupied and virtual states) and vibration frequencies.

1. Introduction

The Coupled Perturbed Hartree-Fock (CPHF) method has recently been implemented in a development version of the CRYSTAL06 code for systems periodic in 1-3 dimensions has been generalized to Density Functional Hamiltonians (CPKS, Coupled Perturbed Kohn-Sham). The dielectric tensor of Magnesium Oxide, Diamond, and Silicon is calculated with four different Hamiltonians, ranging from DFT, in the local density and gradient corrected approximations, to “hybrid” functional B3LYP and Hartree-Fock. The effect of the computational parameters (Pack-Monkhorst net and basis set) is explored. DFT is shown to perform generally better than HF, as it is the case for other properties such as band gaps (which influence the CPHF and CPKS equations via the energy difference between occupied and virtual states) and vibration frequencies.

\begin{equation}
\hat{\Omega}(\mathbf{k}) = i\mathbf{E}^0 \cdot e^{i\mathbf{k} \cdot \mathbf{r}} \nabla_{\mathbf{k}} e^{-i\mathbf{k} \cdot \mathbf{r}}
\end{equation}

with \( \mathbf{r} \) and \( \mathbf{k} \) representing any point in the real and reciprocal space, respectively. Although \( \hat{\Omega} \), first proposed by Blount [8], does not correspond to the real potential generated by an external electric field, it represents, however, a good approximation to the real potential for nonconducting systems [8, 9] with the advantage of being bounded and consistent with the system periodicity. As the total energy of the system immersed in the field of eq. 1 can be expanded into a perturbative series of the field components (denoted by indices \( t, u \) and \( v \)),

\begin{equation}
E_{tot} = E_{tot}^{(0)} - \sum_t \mu_t \xi_t^{(0)} - \frac{1}{2} \sum_{t,u} \alpha_{tu} \xi_t^{(0)} \xi_u^{(0)} - \frac{1}{3!} \sum_{t,u,v} \beta_{tuv} \xi_t^{(0)} \xi_u^{(0)} \xi_v^{(0)} + \ldots
\end{equation}
where $E_{\text{tot}}^{(0)}$ is the total energy of the unperturbed system. All tensors of increasing rank in eq. 2, such as the permanent electric dipole moment ($\mu$), the polarizability ($\alpha$), the hyperpolarizability ($\beta$), can be computed by subsequent derivation of $E_{\text{tot}}$ 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 in CRYSTAL is based on the CPHF equations proposed by Hurst and Dupuis [10] and adapted to the periodic boundary condition context [4, 5]. All equations refer to a local basis set consisting of Gaussian-type atomic orbitals. The details of our implementation were illustrated in previous papers [11, 12]. The calculation of the cell polarizability tensor components for a set of test cases showed that the method is equally accurate and suitable for the treatment of 0-, 1-, 2- and 3-dimensional systems. It was shown in another paper [13] that this method is also applicable to the calculation of optical properties of large unit cell systems with high efficiency, especially because of full use of symmetry. This represents an important advance in quantum \emph{ab initio} modelling of electric field effects in real scale solids, whereas all previous calculations reported in the literature, either based on the same method [6, 7, 14] or alternative methods, like the Modern Theory of Polarization [15, 16, 17], referred to special cases like polymers or small unit cell 3-dimensional crystals.

Nevertheless, the demonstrated high numerical accuracy of our computed results did not correspond to a good estimate of the polarizability values measured experimentally, not because of shortcomings in the Coupled Perturbed method, but rather for inadequacy of the HF approximation in this kind of application, where differences between energy eigenvalues are part of the perturbative formulae (as shown in the next section) and it is well known that HF largely overestimates band gaps. For this reason, we reconsider some steps of the computational scheme in order to show how the CPHF method has been extended to Density Functional Theory (DFT). In the present paper we summarize the equations for the calculation of the polarizability tensor with the Coupled Perturbed Kohn-Sham (CPKS) technique and, in general, address to those contributions in the Hamiltonian, appearing explicitly both in the CPHF and CPKS equations, that were referred to collectively as two-electron integrals in Ref. [12], without specification of any detail about the special treatment of long-range interactions which makes periodic boundary calculations feasible and efficient. Improvement in the accuracy of the static polarizability calculated with CPKS over CPHF is shown for an insulator (MgO) and two typical semiconductors (C, Si). Dependence of accuracy on the main computational parameters, such as basis set, choice of DFT exchange-correlation functional and integration grid in reciprocal space is discussed.

2. The method

The components of the second rank polarizability tensor for a periodic system in a local basis set can be calculated as second derivatives of the total energy (eq. 2) relative to the various components of the electric field [10, 5, 4, 12]. This can be done in terms of real space matrix elements:

$$
\alpha_{tv} = -2 \sum_{\mu,\nu, g} D^t_{\mu\nu} \Omega^g_{\mu\nu} \Omega^v_{\mu\nu}
$$

(3)

where the sums extend to the atomic orbital (AO) pairs $\varphi^0_\mu$ and $\varphi^g_\nu$, the first AO being centered in the origin cell and the latter in the lattice cell located at real lattice vector $g$; $D^t$ is the first derivative of the unperturbed density matrix resulting from the SCF calculation with respect to the $t$th component of the applied electric field; $\Omega^v$ is the $v$th component of the perturbation matrix (expectation value of the perturbative operator in eq. 1 for every AO pair).

The calculation of $\Omega^v$ matrix elements, although slightly involved, follows straightforwardly from the eigenvalues and eigenvectors of the unperturbed system. The reader can find all details about
it with consistent notation in Ref. [12]. On the contrary, the calculation of the density matrix derivatives requires a self-consistent iterative procedure known as the Coupled Perturbed scheme. As outlined in Ref. [12], every density matrix element, expressed in terms of the eigenvectors of the unperturbed system (sum over occupied states, SOS) and their derivatives relative to the electric field components,

\[ D_{\mu\nu}^k = \sum_{k} e^{i k \cdot g} \sum_{\text{occ}} (C^t_{\mu i}(k)^* C_{\nu i}(k) + C_{\mu i}(k)^* C^t_{\nu i}(k)) \]  

(4)

can only be calculated if the electric field derivatives of the eigenvectors \((C^t)\) are known. \(C^t\) are obtained by unitary transformation of \(C\) through matrix \(U^t\) to be determined:

\[ C^t(k) = C(k)U^t(k) \]

(5)

Thus, the effect of the application of an external electric field is fully accounted for by the modification in the Crystalline Orbitals (CO) of the unperturbed system introduced by \(C^t\). \(U^t\) is defined in the basis of the COs as

\[ U^t_{ij}(k) = \frac{G^t_{ij}(k)}{E_j(k) - E_i(k)} \]

(6)

like in the molecular case [10], with \(G^t_{ij}\), the derivative of \(F_{ij}\) (the Fock/Kohn-Sham matrix element between the \(i\)th and the \(j\)th CO) with respect to the \(t\)th component of the applied electric field, being scaled to the difference between the corresponding eigenvalues of the unperturbed system, \(E_i(k)\) and \(E_j(k)\). Because the perturbed wavefunction is invariant to unitary transformation within the occupied manifold, \(i\) and \(j\) in eq. 6 refer to occupied and virtual states, respectively. The appearance of the eigenvalues in the formula for \(U^t\) requires that also \(G^t\) in eq. 6 be represented in the basis of COs. However, in CRYSTAL, \(F\) is first calculated in the AO basis and then Fourier transformed to the basis of the COs, and so are its derivatives.

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 LDA (Local Density Approximation), GGA (Generalised Gradient Approximation) or HF can be considered particular cases of that more general case. Hybrid functionals incorporate a fraction \(\alpha_X\) of “exact” exchange \((f_{X}^{HY})\) and a complementary fraction of exchange functional of the density \((f_{DF}^{X})\), which can be summed to the correlation part of the density functional \((f_{DF}^{X})\) to give

\[ f^{XC} = \alpha_X f^{X}_{HY} + (1 - \alpha_X) f^{X}_{DF} + f^{C}_{DF} \]  

(7)

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

We focus on \(F_{e-e}\), the electron-electron repulsive interaction part of \(F\), as the other contributions to \(F\), i.e. the kinetic energy and electron-nuclear attraction integrals evaluated with reference to the AO's are not affected by the field (they contain no dependence on the density matrix and AO's are not affected by the field, these being the basis functions of the variational basis set) [10, 12, 13] and field derivatives are null. On the contrary, \(F_{e-e}\) depends explicitly on the density matrix and, according to eq. 6, the change of the system operated by the perturbing field is contained in the derivatives of the density matrix. \(F_{e-e}\) in CRYSTAL, with the choice of a hybrid-functional DFT approximation, would include the following terms:

\[ F_{e-e} = F_{sr}^{C} + F_{wo}^{C} + F_{lr}^{C} + \alpha_X (F_{sr}^{X} + F_{wo}^{X}) + F_{DF}^{XC} \]

(8)
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 their mutual interaction, i.e. short-range interactions \( \mathbf{F}_{sr} \), weakly overlapping electron distributions within a defined quantum radius \( \mathbf{F}_{wo} \), long-range interactions \( \mathbf{F}_{lr} \). Similarly, exchange contributions are subdivided into short-range \( \mathbf{F}_X^{sr} \) and longer-range interactions \( \mathbf{F}_X^{wo} \). The rest comes from the exchange-correlation functional of the electron density and its gradient.

We now consider all terms in eq. 8 for one general element of the \( \mathbf{F}^{ee} \) matrix in more details:

a. Only interactions between overlapping electron distributions are evaluated as actual two-electron Coulomb integrals

\[
[F_{sr}]^{g}_{\mu
u} = \sum_{\rho, \tau} \sum_{g'}^{\infty} D_{\rho\tau}^{g'} \sum_{g''}^{\infty} \langle \varphi_{\mu \rho}^{0} \varphi_{\nu \tau}^{0} | \varphi_{\rho \tau}^{g'} \varphi_{\rho \tau}^{g''} \rangle
\]  

(9)

b. Integrals relative to weakly overlapping electron distributions within the so called “quantum zone” are evaluated through multipolar expansions, \( \gamma_{\ell m}(\mu \nu g) \) and \( \gamma_{\ell m}(\rho \tau g') \), of the two electron distributions at their respective centroids coupled by potential terms \( V_{\ell m}^{\rho \tau} \) with the same quantum numbers \( \ell, \ell', m \) and \( m' \)

\[
[F_{wo}]^{g}_{\mu
u} = \sum_{\ell, \ell', m, m'} \gamma_{\ell m}(\mu \nu g) \sum_{\rho, \tau} \sum_{g'} V_{\ell m}^{\rho \tau}(\mu \nu \rho \tau g' g) D_{\rho \tau}^{g'} \gamma_{\ell m}(\rho \tau g')
\]  

(10)

the sum over \( g'' \) lattice vectors being included in \( V_{\ell m}^{\rho \tau} \).

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, \( \Phi_{\ell m}^{n}(\mu \nu g, A) \), saturated by \( \Gamma_{\ell m}^{n}(A) \):

\[
[F_{lr}]^{g}_{\mu
u} = \sum_{A} \sum_{\ell, m} \Gamma_{\ell m}^{n}(A) \Phi_{\ell m}^{n}(\mu \nu g, A)
\]  

(11)

Only \( \Gamma_{\ell m}^{n}(A) \) multipoles contain explicit dependence on the density matrix:

\[
\Gamma_{\ell m}^{n}(A) = \sum_{\mu \in A, \nu \in A} \sum_{\nu' \in A} D_{\nu \nu'}^{g} \gamma_{\ell m}^{n}(\mu \nu' g)
\]  

(12)

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

\[
[F_{sr}]^{g}_{\mu
u} = -\frac{1}{2} \sum_{\rho, \tau} \sum_{g'}^{\infty} D_{\rho\tau}^{g'} \sum_{g''}^{\infty} \langle \varphi_{\mu \rho}^{0} | \varphi_{\nu \tau}^{0} \varphi_{\rho \tau}^{g'} \varphi_{\rho \tau}^{g''} \rangle
\]  

(13)

e. Exchange integrals involving weakly overlapping electron distributions are approximated by coupling multipolar expansions like in case b (eq. 10):

\[
[F_{wo}]^{g}_{\mu
u} = -\frac{1}{2} \sum_{\ell, m} \sum_{\rho} \sum_{g'} \gamma_{\ell m}(\mu \rho g') D_{\rho\tau}^{g'} \sum_{\ell', m'} \sum_{g''} V_{\ell m}^{\rho \tau}(\mu \nu \rho \tau g' g) \gamma_{\ell m}(\rho \tau g' g'')
\]  

(14)
f. Following Pople et al. [19], the DFT exchange-correlation part of the Fock-matrix is calculated by the following formula:

$$\mathbf{F}_{DFT}^{XC} = \sum_{i} u_{i} \left[ \frac{\partial f^{XC}}{\partial \rho} \phi_{\mu}^{0}(r_{i}) \phi_{\nu}^{\delta}(r_{i}) + 2 \frac{\partial^{2} f^{XC}}{\partial \rho \partial |\nabla \rho|^{2}} \nabla \rho \cdot \nabla \phi_{\mu}^{0}(r_{i}) \phi_{\nu}^{\delta}(r_{i}) \right] \mathbf{r}_{i} \right],$$

(15)

The contributions in eq. 15 are evaluated at points $r_{i}$ of a grid and summed (numerical integration). Each grid point is associated with a geometrical weight $w_{i}$ according to an atomic partition [20]. An efficient computational scheme for the implementation of eq. 15 was proposed by Treutler and Ahlrichs [21]. For all terms in eq. 8, except $\mathbf{F}_{DFT}^{XC}$, the derivatives with respect to the components of the applied field are obtained simply by replacing the density matrix elements in eqs. 9-14 with those of the corresponding density matrix elements with respect to the field. The DFT exchange-correlation part depends on the density matrix elements through the electron density, which is expressed at each point $r_{i}$ as

$$\rho(r_{i}) = \sum_{\mu, \nu} \sum_{g} D_{\mu \nu}^{g} \phi_{\mu}^{0}(r_{i}) \phi_{\nu}^{g}(r_{i})$$

(16)

where sums extend to all atomic orbitals contributing to the electron density at $r_{i}$. Also in this case, the derivative of the density with respect to the $t$th component of the applied field ($\rho^{t}$) is obtained simply by replacing all $D_{\mu \nu}^{g}$ elements with $D_{\mu \nu}^{g t}$ in eq. 16. The same rule holds for the field derivative of the density gradient ($\nabla \rho^{t}$), because the two derivation variables are independent of each other. However, the full derivative of eq. 15 is complicated by the dependence of the functional on the density [22]:

$$\left[ \mathbf{F}_{DFT}^{XC} \right]_{\mu \nu}^{t} = \sum_{i} u_{i} \left\{ 2 \frac{\partial f^{XC}}{\partial \rho} \rho^{t} + 2 \frac{\partial^{2} f^{XC}}{\partial \rho \partial |\nabla \rho|^{2}} \nabla \rho \cdot \nabla \rho^{t} \right\} \phi_{\mu}^{0}(r_{i}) \phi_{\nu}^{g}(r_{i}) + 2 \frac{\partial^{2} f^{XC}}{\partial \rho \partial |\nabla \rho|^{2}} \nabla \rho \cdot \nabla \phi_{\mu}^{0}(r_{i}) \phi_{\nu}^{g}(r_{i}) + 2 \frac{\partial f^{XC}}{\partial \rho} \rho^{t} \right\} \phi_{\mu}^{0}(r_{i}) \phi_{\nu}^{g}(r_{i}) + 2 \frac{\partial^{2} f^{XC}}{\partial \rho \partial |\nabla \rho|^{2}} \nabla \rho \cdot \nabla \phi_{\mu}^{0}(r_{i}) \phi_{\nu}^{g}(r_{i}) \right\} \mathbf{r}_{i} \right],$$

(17)

Weights $w_{i}$ are purely geometric entities and do not depend on the applied field, nor do the atomic orbitals. At difference with eq. 15, second derivatives of the exchange-correlation density functional appear in eq. 17 and the corresponding new routines had to be coded. However, we benefited the comparison with routines in the Daresbury repository [23], that were generated automatically on the base of Knowles’s prescriptions [24]. Instead, from a computational point of view, eqs. 15 and 17 have the same logical structure, so that the use of the routines for the SCF calculation can be extended to CPKS easily, provided the correct contributions are included in the formula.

### 3. 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. In a 3-dimensional crystal, the dielectric tensor components are proportional to the corresponding components of the polarizability tensor (eq. 3) through the following relation:

$$\varepsilon_{tv} = \delta_{tv} + 4 \pi V^{-1} \alpha_{tv}$$

(18)

with $V$ denoting the unit cell volume. Therefore, the $\varepsilon_{tv}$ component of the dielectric tensor depends on the derivative of the density matrix, $\mathbf{D}^{t}$, and the perturbative matrix $\Omega^{v}$, as stated
in eq. 3. Both the density matrix derivatives and the $\Omega^t$ matrices are strongly affected by the system band structure, as differences of unperturbed CO energies appear in the definition of both [12]. For example, differences between occupied and virtual orbital energies appear at the denominator of eq. 6 to define matrix $U$ operating a unitary tranformation of the unperturbed eigenvectors to the perturbed eigenvectors, in terms of which the $D^t$ matrices are expressed (eqs. 4-5). It is then to be expected that well determined band gaps are crucial for the accurate calculation of the $\alpha$ and $\epsilon$ tensors, particularly for small gap compounds, where the denominator in eq. 6 is correspondingly small and large $U$ 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 different Hamiltonians, and LDA (Local Density Approximation), 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 dielectric tensor components and LDA large values. For this reason we calculate the dielectric tensor of compounds differing for their band structures, namely Magnesium Oxide, Diamond, and Silicon, i.e. a large-gap ionic system (7.8 eV), a large-gap semiconductor (5.5 eV), and a small-gap semiconductor (vertical gap: 3.5 eV), respectively.

We first examine the effect of the basis set extension on the determination of the dielectric constant of MgO in Table 1 ($\epsilon$ of cubic systems contains only one independent component). Basis set A is of triple-$\zeta$ quality (exponents in Bohr$^{-2}$), with $\alpha_{\text{Mg}} = (0.69, 0.30)$ and $\alpha_{\text{O}} = (0.50, 0.185)$. A double-$\zeta$ basis set was not considered here, because it is not flexible enough for a good estimate of either energy or $\epsilon$. The addition of one polarization function per atom is important. Nevertheless, the $d$ shell added to Mg (basis set B, $\alpha = 0.65$) has a stronger effect on $E_{\text{tot}}^0$ than the $d$ polarization shell added to O (basis set C, $\alpha = 0.60$), whereas the relative importance of the two polarization functions is reversed in the case of $\epsilon$. While two sets of $d$ shells per atom (basis set D, $\alpha_{\text{Mg}} = 1.75, 0.4$ and $\alpha_{\text{O}} = 1.10, 0.19$) still improve $E_{\text{tot}}^0$, but to a minor extent, they do increase the value of $\epsilon$ significantly, by about 15%. On the contrary further addition of one $f$ polarization per atom (basis set E, $\alpha_{\text{Mg}} = 0.4$, $\alpha_{\text{O}} = 0.7$) has a secondary effect on $\epsilon$. Overall, the correction on $\epsilon$ operated by the Coupled Perturbed method over the value obtained with the SOS approximation becomes more important with the more flexible basis sets and it is larger with HF than B3LYP.

Concerning the semiconductors, a double-$\zeta$ basis set (A), derived from standard Pople’s 6-21G with $\alpha = 0.225$ for the outer $sp$ shell, was used for Diamond (Table 1), for it possesses a close-packed structure. Basis set A was progressively augmented by one (basis set B, $\alpha = 0.9$) and two (basis set C, $\alpha = 1.5, 0.65$) sets of $d$ polarization functions, and finally one set of $f$ AOs (basis set D, $\alpha = 0.7$). For Silicon (Table 1), we considered, initially, a triple-$\zeta$ basis set (A) from Ref. [25] with $\alpha = (0.31, 0.145)$ for the outer $sp$ shells. Addition of one (basis set B, $\alpha = 0.42$) and two (basis set C, $\alpha = 1.2, 0.3$) sets of $d$ polarization functions, as well as one further set of $f$ functions (basis set D, $\alpha = 0.8$) was also considered. As for MgO, Table 1 shows that extension of the basis set leads to an increase in the estimate of $\epsilon$ and polarization functions are important, particularly $d$ polarization functions, but even the inclusion of $f$ AOs is non-negligible for these semiconductors. By comparing these values of $\epsilon$ with those for MgO, we see that the importance of the correction due to the CPKS/CPHF over the SOS values increases with the decrease in the band gap.

Four different Hamiltonians were considered, namely LDA (Slater/Vosko-Wilk-Nusair), GGA (Becke/Lee-Yang-Parr), hybrid Becke’s three-parameter B3LYP and HF. B3LYP, which is known to provide band gap values intermediate between LDA/GGA and HF and usually very close to the experimental values [26], predicts the following valence-conduction vertical gaps in $\Gamma$: 7.3, 5.7 and 2.0 eV for MgO, C and Si, respectively. The values of $\epsilon$ reported in Table 2 were all calculated at the experimental geometry with basis sets including a double set of $d$ polarization.
Table 1. Dependence of the dielectric constants of Magnesium Oxide, Diamond, and Silicon on the basis sets with HF and B3LYP approximations. A shrinking factor $S = 8$ is used along every reciprocal basis vector for the Pack-Monkhorst net, corresponding to 29 asymmetric $\mathbf{k}$ points with full symmetry and 59 $\mathbf{k}$ points after application of the electric field. Coulomb and exchange series were truncated according to standard values of thresholds (6, 6, 6, 6, 12) for MgO and C, and to values 7, 7, 7, 7, 14 for Si. The total energy ($\Delta E_{tot}^0$, in mHa) is referred to the total energy of the corresponding compound computed with the most extended basis set considered, including $d$ and $f$ polarization functions ($E_{tot}^{0\text{HF}} = -274.682809, -75.716122, -577.929790$ Ha for MgO, C, and Si, respectively, and $E_{tot}^{0\text{B3LYP}} = -275.457008, -76.135364, -578.983638$ Ha). $\epsilon_{SOS}$ obtained with the sum-over-state approximation are reported for comparison with the values of $\epsilon$ calculated with CPHF and CPKS.

<table>
<thead>
<tr>
<th>Basis sets</th>
<th>MgO</th>
<th>C</th>
<th>Si</th>
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<tr>
<td></td>
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<td></td>
<td>C</td>
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<td>$\epsilon_{SOS}^{\text{CPKS}}$</td>
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</tbody>
</table>

Table 2. Dielectric constant of Magnesium Oxide, Diamond, and Silicon calculated with different choices of Hamiltonian and shrinking factor $S$ of the Pack-Monkhorst net. Symbols and units as in Table 1. The basis sets used are D for MgO and C for Diamond and Silicon.

<table>
<thead>
<tr>
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<th>B3LYP</th>
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</tbody>
</table>
functions (basis set D for MgO and C for Diamond and Silicon, in Table 1) for the four different Hamiltonians and different densities of the Pack-Monkhorst net. Analysis of the data for MgO points out that B3LYP approximates the experimental value of $\epsilon = 2.95$ [27] very well. As expected, LDA and GGA overestimate it approximately in the same way as they underestimate the band gap (about 5.1 eV vs. 7.8 eV), whereas HF underestimates $\epsilon$ by more than 15% (HF valence-conduction gap: 15.9 eV). The choice of shrinking factor $S$ is not critical, but $S = 4$ is insufficient to yield well converged results. Data obtained with $S = 16$ are not reported in the case of MgO, as they are identical to $S = 12$. In the cases examined, the Couple-Perturbed calculation corrects the uncoupled value of $\epsilon$ from the SOS in the “right” direction, by increasing it in the case of HF and B3LYP and, on the contrary, by decreasing it for LDA and GGA.

The experimental values of $\epsilon$ are 5.7 for Diamond and 11.8 for Silicon [28]. Performance assessment of the four Hamiltonians is less neat in the case of these semiconductors. However, the general trends are the same as for MgO. LDA and GGA approximate the experimental values of $\epsilon$ extremely well, despite underestimating the valence-conduction band gap considerably (4.0 vs 5.5 eV for Diamond and 0.7-0.8 vs 3.5 eV for Silicon), whereas B3LYP predictions (5.7 eV for C and 2.0 eV for Si) approach the experimental gap values better than LDA and GGA, but $\epsilon$ is slightly worse. The dependence on the Pack-Monkhorst grid density is larger with these smaller-gap compounds than with MgO and the change in $\epsilon$ from $S = 8$ to $S = 12$ still accounts for 0.25% of its value. The number of cycles required to reach convergence on $\epsilon$ within the fourth decimal figure in the self-consistent CPHF/CPKS varies in the range of 9-25 and seems to be related to band gap widths and the entity of the correction over the SOS values, though not in a clear-cut way.

References
[23] van Dam H www.cse.scitech.ac.uk/ccg/dft