Comparison of the polarizability of periodic systems computed by using the length and velocity operators

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Abstract. The theorem relating the length (L) and velocity (V) operators, that permits to compute in two alternative ways the polarizabilities of finite systems, is generalized to periodic infinite cases. The two alternative strategies have been implemented in the CRYSTAL code, that uses Gaussian type basis sets, within the CPHF and CPKS formalisms. The dielectric constant of diamond, SiC, silicon and MgO has been obtained with four different hamiltonians (HF, LDA, PBE, B3LYP). The effect of basis set and other computational parameters are discussed. It turns out that when a relatively extended basis set is used, LDA and PBE results obtained with the L and V operators nearly coincide, whereas HF and B3LYP schemes provide different results, as expected on the basis of the non-commutability of the HF-exchange and length operators.

1. The scalar potential or length (L) gauge.
In the presence of an electric field, the single-particle Hamiltonian operator takes the form:

\[ H = \frac{1}{2m} (\vec{p}_e - e \vec{A}(\vec{r}, t))^2 + e \phi(\vec{r}, t) + V_C(\vec{r}) \] (1)

where \( \vec{p}_e = \frac{\hbar}{i} \nabla \) is the momentum of the electron, \( \vec{r} \) its position, \( \vec{A}(\vec{r}, t) \) and \( \phi(\vec{r}, t) \) the vector and scalar potentials defining the electric field \( \vec{F} \) as:

\[ \vec{F} = -\nabla \phi - \frac{\partial \vec{A}}{\partial t} \] (2)

and \( V_C(\vec{r}) \) the Coulomb potential energy in the absence of outer field.

An appropriate choice of the gauge permits to reduce the field expression to the first (scalar potential) or second (vector potential) term only. In the former case (\( \phi \) only), when the field is static (low frequency limit, or \( \omega = 0 \)) and for a fixed momentum \( \vec{q} \), we can write (see Refs. [1, 2]):

\[ \phi(\vec{r}) = \phi_0(\vec{q}) e^{iq \cdot \vec{r}} \] (3)

so that the field becomes:

\[ \vec{F}(\vec{r}) = -i\vec{q}\phi_0 e^{iq \cdot \vec{r}} = \vec{F}_0 e^{iq \cdot \vec{r}} \] (4)
from which we obtain for $\phi_0$:

$$\phi_0 = i e \vec{F}_0 \cdot \frac{\vec{q}}{q^2}$$  \hspace{1cm} (5)

Then, the transition moments between occupied and virtual states involved in the calculation of polarizability, in the general case of a periodic system, take the form:

$$\langle \Psi_{i,\vec{k}} | e^{i q \cdot \vec{r}} | \Psi_{j,\vec{k}'} \rangle = i e \vec{F}_0 \cdot \frac{\vec{q}}{q^2} \langle \Psi_{i,\vec{k}} | e^{i q \cdot \vec{r}} | \Psi_{j,\vec{k}'} \rangle$$  \hspace{1cm} (6)

where $\Psi_{i,\vec{k}}$ is the crystalline orbital associated to the $\epsilon_{i,\vec{k}}$ eigenvalue characterizing each $\vec{k}$-point of the first Brillouin zone [3]. $\Psi_{i,\vec{k}}$ (as any Bloch function) can be written as the product of a periodic function $u_{i,\vec{k}}$ times a phase factor $e^{i \vec{k} \cdot \vec{r}}$, so that the matrix elements in eq. 6 take the form

$$\vec{F}_0 \cdot \vec{\mu}_{ij}(\vec{k},\vec{k}') = i e \vec{F}_0 \cdot \frac{\vec{q}}{q^2} \langle u_{i,\vec{k}} | e^{-i \vec{k} \cdot \vec{r}} e^{i q \cdot \vec{r}} e^{-i \vec{k}' \cdot \vec{r}} | u_{j,\vec{k}'} \rangle$$  \hspace{1cm} (7)

According to momentum conservation, these integrals are null except when $\vec{k} - \vec{k}' = \vec{q}$. In the case of a field constant in space ($\vec{q} \rightarrow \vec{0}$), a limited development of $e^{i q \cdot \vec{r}}$ and $| \Psi_{j,\vec{k} - \vec{q}} \rangle$ to the first order in $\vec{q}$, leads to (for $i \neq j$) [4]:

$$\vec{F}_0 \cdot \vec{\mu}_{ij}(\vec{k},\vec{k}') = i \lim_{\vec{q} \rightarrow 0} e \vec{F}_0 \cdot \frac{\vec{q}}{q^2} \langle u_{i,\vec{k}} | 1 + i \vec{q} \cdot \vec{r} | u_{j,\vec{k}} - \vec{q} \cdot \vec{\nabla}_{\vec{k}} u_{j,\vec{k}} \rangle = -e \vec{F}_0 \cdot \langle u_{i,\vec{k}} | \vec{r} + i \vec{\nabla}_{\vec{k}} u_{j,\vec{k}} \rangle$$  \hspace{1cm} (8)

The perturbation operator $\vec{r} + i \vec{\nabla}_{\vec{k}}$ can be written in an alternative and more elegant form (see ref. [5]):

$$\vec{\Omega}_{\vec{k}} = \vec{r} + i \vec{\nabla}_{\vec{k}} = i e \vec{k} \cdot \vec{r}$$  \hspace{1cm} (9)

as easily verified by considering the effect of the right hand form of the operator in eq. 9 on the periodic function $u_{i,\vec{k}}$.

It should be noticed that, as the field is constant in space ($\vec{q} \rightarrow \vec{0}$), the momentum conservation condition (see eq. 7) reduces to $\vec{k} = \vec{k}'$; in other words, $\vec{\Omega}_{\vec{k}}$ maintains the block-diagonal form of the hamiltonian matrix with respect to different $\vec{k}$ vectors, with an enormous simplification from the computational point of view. This feature remains valid for frequency dependent fields ($\omega \neq 0$); it remains valid also for fields varying in space periodically, with a period equal to a multiple of any linear combination of the three lattice vectors of the unit cell; in this latter case a new unit cell must be defined accordingly.

At variance with respect to the dipole moment, the polarization vector, i.e. the variation of the dipole moment of the infinite system with respect to the perturbing electric field, is a well defined quantity. The polarizability tensor $\alpha$, which corresponds to the second-order perturbation energy, requires the evaluation of matrix elements of the transition moment between the ground and excited states.

For a multi-electronic system described by a single Slater determinant, the polarizability components take the form (see Refs. [6, 4]):

$$\alpha_{uv}^L = \frac{4e^2}{N} \sum_{\vec{k}}^{occ} \sum_i^{vir} \sum_j^{vir} \langle \Psi_{i,\vec{k}} | r_u + i \nabla_{\vec{k}_u} | \Psi_{j,\vec{k}} \rangle \langle \Psi_{j,\vec{k}} | r_v + i \nabla_{\vec{k}_v} | \Psi_{i,\vec{k}} \rangle$$

$$\epsilon_{j,\vec{k}} - \epsilon_{i,\vec{k}}$$  \hspace{1cm} (10)
where $\Psi_{i,\vec{k}}$ is a crystalline orbital and $\epsilon_{i,\vec{k}}$ is the corresponding eigenvalue at $\vec{k}$. The above equation corresponds to the so-called SOS (sum over states) solution using the length operator $\langle L \rangle$ as defined in equation 9.

In the molecular case, the wave-function does not depend on the $\vec{r}$ vector ($\Psi_{0(n),\vec{k}} \equiv \Psi_{0(n)}$), so that repeating the expansion of the exponential factor that leads to eq. 8, the usual electric dipole approximation $e\vec{r} \cdot \vec{F}$ is obtained for a static uniform electric potential. As regards the polarizability tensor, the operator $\nabla_{\vec{k}}$ disappears, and we retrieve again the well-known expression of the polarizability for finite systems at the first step of the coupled perturbed Hartree-Fock (CPHF) calculation (see Ref. [7]).

In the case of periodic systems, the presence of the gradient operator $\nabla_{\vec{k}}$ in the definition of the perturbation introduces a certain degree of difficulty in the calculation of electric properties, as gradients with respect to the electric field and $\vec{k}$ vectors must be taken into account at the various levels of theory. For this reason it might be interesting to use the alternative definition, where the length operator containing the $\nabla_{\vec{k}}$ operator, is substituted by $\nabla_{\vec{r}}$ (velocity operator $V$), that is the gradient with respect to the direct space position $\vec{r}$.

### 2. From the $L$ ($\nabla_{\vec{k}}$) to the $V$ ($\nabla_{\vec{r}}$) Operators.

In order to obtain the $V$ form of the electric field operator, let us consider the commutator between $H_0$ (that contains a kinetic and a Coulomb plus exchange term $U(\vec{r})$) and the general expression of the electric scalar potential given in eq 3: $\phi(\vec{r}) = \phi_0 e^{i\vec{q} \cdot \vec{r}}$.

If we suppose that $U(\vec{r})$ and $\phi(\vec{r})$ commute, we can write:

$$[H_0, \phi(\vec{r})] = \frac{-\hbar^2}{2m} [\nabla_{\vec{r}}, \phi_0 e^{i\vec{q} \cdot \vec{r}}] = \frac{-\hbar^2}{2m} \phi_0 [\nabla^2_{\vec{r}}, e^{i\vec{q} \cdot \vec{r}}]$$

(11)

The action of $\nabla^2_{\vec{r}}$ on $e^{i\vec{q} \cdot \vec{r}}$ leads to:

$$\nabla^2_{\vec{r}} e^{i\vec{q} \cdot \vec{r}} = \nabla_{\vec{r}} \cdot (i\vec{q} e^{i\vec{q} \cdot \vec{r}} + e^{i\vec{q} \cdot \vec{r}} \nabla_{\vec{r}}) = e^{i\vec{q} \cdot \vec{r}} (-\vec{q} \cdot \vec{q} + 2i\vec{q} \cdot \nabla_{\vec{r}} + \nabla^2_{\vec{r}} - \nabla_{\vec{r}} \cdot \nabla_{\vec{r}})$$

(12)

and, then, to:

$$[\nabla^2_{\vec{r}}, e^{i\vec{q} \cdot \vec{r}}] = e^{i\vec{q} \cdot \vec{r}} (-q^2 + 2i\vec{q} \cdot \nabla_{\vec{r}})$$

(13)

We can use this expression for computing the integral of the commutator between two different crystalline orbitals $\Psi_{i,\vec{k}}$ and $\Psi_{j,\vec{k}'}$ (they are eigenvectors of $H_0$, with eigenvalues $\epsilon_i(\vec{k})$ and $\epsilon_j(\vec{k}')$, respectively):

$$\langle \Psi_{i,\vec{k}} | [H_0, e^{i\vec{q} \cdot \vec{r}}] | \Psi_{j,\vec{k}'} \rangle = \frac{-\hbar^2}{2m} \langle \Psi_{i,\vec{k}} | e^{i\vec{q} \cdot \vec{r}} (-q^2 + 2i\vec{q} \cdot \nabla_{\vec{r}}) | \Psi_{j,\vec{k}'} \rangle$$

(14)

As regards the left member, by applying $H_0 e^{i\vec{q} \cdot \vec{r}}$ to the bra $\langle \Psi_{i,\vec{k}} |$ and $e^{i\vec{q} \cdot \vec{r}} H_0$ to the ket $| \Psi_{j,\vec{k}'} \rangle$, we have:

$$\langle \Psi_{i,\vec{k}} | [H_0, e^{i\vec{q} \cdot \vec{r}}] | \Psi_{j,\vec{k}'} \rangle = \langle \Psi_{i,\vec{k}} | H_0 e^{i\vec{q} \cdot \vec{r}} - e^{i\vec{q} \cdot \vec{r}} H_0 | \Psi_{j,\vec{k}'} \rangle = (\epsilon_i - \epsilon_j) \langle \Psi_{i,\vec{k}} | e^{i\vec{q} \cdot \vec{r}} | \Psi_{j,\vec{k}'} \rangle$$

(15)

so that the following equality is obtained:

$$\frac{-\hbar^2}{2m} \langle \Psi_{i,\vec{k}} | e^{i\vec{q} \cdot \vec{r}} (-q^2 + 2i\vec{q} \cdot \nabla_{\vec{r}}) | \Psi_{j,\vec{k}'} \rangle = (\epsilon_i - \epsilon_j) \langle \Psi_{i,\vec{k}} | e^{i\vec{q} \cdot \vec{r}} | \Psi_{j,\vec{k}'} \rangle$$

(16)

As for eq. 7, momentum conservation imposes that $\vec{k}' = \vec{k} - \vec{q}$. 


In the limit $\vec{q} \to \vec{0}$, the development of $\Psi_{j,\vec{k}-\vec{q}}$ to the first order in $\vec{q}$:

$$\Psi_{j,\vec{k}-\vec{q}} \simeq \Psi_{j,\vec{k}} - \vec{q} \cdot \vec{\nabla}_k \Psi_{j,\vec{k}}$$

as well as the developments $\epsilon_{j,\vec{k}-\vec{q}} \simeq \epsilon_{j,\vec{k}}$ and $e^{i \vec{q} \cdot \vec{r}} \simeq 1 + i \vec{q} \cdot \vec{r}$, lead to, for the left-hand member of eq. 16:

$$-\frac{\hbar^2}{2m} \langle \Psi_{i,\vec{k}} | (1 + i \vec{q} \cdot \vec{r}) (-\vec{q}^2 + 2i \vec{q} \cdot \vec{\nabla}_r) | \Psi_{j,\vec{k}} \rangle \simeq -\frac{\hbar^2}{m} i \vec{q} \cdot \langle \Psi_{i,\vec{k}} | \vec{\nabla}_r | \Psi_{j,\vec{k}} \rangle$$

(17)

and, for the right-hand member of the same equation for $i \neq j$:

$$\langle \epsilon_{i,\vec{k}} - \epsilon_{j,\vec{k}} + \vec{q} \cdot \vec{\nabla}_k \epsilon_{j,\vec{k}} | \langle i | 1 + i \vec{q} \cdot \vec{r} | \Psi_{j,\vec{k}} - \vec{q} \cdot \vec{\nabla}_k \Psi_{j,\vec{k}} \rangle \simeq (\epsilon_{i,\vec{k}} - \epsilon_{j,\vec{k}}) i \vec{q} \cdot \langle \Psi_{i,\vec{k}} | \vec{r} + i \vec{\nabla}_k | \Psi_{j,\vec{k}} \rangle$$

(18)

Equating the two above expressions, we obtain:

$$-\frac{\hbar^2}{m} \langle \Psi_{i,\vec{k}} | \vec{\nabla}_r | \Psi_{j,\vec{k}} \rangle = (\epsilon_{i,\vec{k}} - \epsilon_{j,\vec{k}}) i \vec{q} \cdot \langle \Psi_{i,\vec{k}} | \vec{r} + i \vec{\nabla}_k | \Psi_{j,\vec{k}} \rangle$$

(19)

The above equation shows that the length ($L$) operator $\Omega_{\vec{k}} = \vec{r} + i \vec{\nabla}_k$ can be replaced by the velocity ($V$) operator $\vec{\nabla}_r$ (or by the more symmetric $\vec{r} + i \vec{k}$ form; note that the effect of $i \vec{k}$ is null as $i \neq j$ in eq. 19) in the calculation of transition moments between different crystalline orbitals referring to the same $\vec{k}$ vector. The well known ([8, 9, 10]) relation between $\vec{r}$ and $\vec{\nabla}_r$ that holds for finite systems is easily retrieved, when remembering that $\vec{\nabla}_r$ is inactive, as molecular orbitals do not depend on $\vec{k}$.

It is important to outline that the L-V equivalence holds under two conditions, namely:

(i) The wave-functions appearing in Eq. 19 are solutions of Schrödinger’s equation (or its projection in a complete basis set). The use of a finite basis set is expected to have a different effect on the (approximated) results obtained in the two ways.

(ii) The potential part of the Hamiltonian operator $H_0$ commutes with $\vec{r}$. This latter condition is satisfied in the case of DFT functionals, both local (LDA) or gradient corrected (GGA), as we are going to use in the following (exchange LDA with correlation VWN: Refs. [11, 12], exchange GGA (Becke): Ref. [13]).

The Hartree-Fock exchange, on the contrary, as well as hybrid functionals containing some fraction of the non local HF exchange potential, as B3LYP [14, 15], that will be used in the following, do not commute with $\vec{r}$ [16]. In this case, the relation must be corrected by the non-zero commutator as it is done in Ref. [17].

The use of $\vec{\nabla}_r$ yields to the following expression for the transition moments between crystalline orbitals (see eq. 8):

$$-\vec{\mu}_{ij}(\vec{k}) = e \langle \Psi_{i,\vec{k}} | \vec{r} + i \vec{\nabla}_k | \Psi_{j,\vec{k}} \rangle = -\frac{\hbar^2}{m} e \langle \Psi_{i,\vec{k}} | \vec{\nabla}_r | \Psi_{j,\vec{k}} \rangle / (\epsilon_{i,\vec{k}} - \epsilon_{j,\vec{k}})$$

(20)

For the calculation of the polarizability, the $i \neq j$ cases only are relevant in the above formula. For the permanent dipole moment, on the contrary, the $i = j$ case should be considered, but the denominator goes to zero. The dipole moment of infinite systems is however an ill defined quantity, and its calculation is not required.

The substitution of the length operator $\Omega(\vec{k})$ by $\vec{\nabla}_r$ according to Eq. 20 in the polarizability expression Eq. 10 leads to the velocity ($V$) polarizability components:

$$\alpha_{uv}^V = -\frac{4e^2 \hbar^4}{N m^2} \sum_{\vec{k}} \sum_{i} \sum_{\text{occ}} \sum_{\text{virt}} \frac{\langle \Psi_{i,\vec{k}} | \vec{\nabla}_r | \Psi_{j,\vec{k}} \rangle \langle \Psi_{j,\vec{k}} | \vec{\nabla}_r | \Psi_{i,\vec{k}} \rangle}{(\epsilon_{j,\vec{k}} - \epsilon_{i,\vec{k}})^3}$$

(21)
at the SOS level of calculation.

At the coupled-perturbed Hartree-Fock (CPHF) or Kohn-Sham (CPKS) level, when relaxation of the orbitals is taken into account, the expressions for $\alpha$ are similar, but include the complete derivative of the Fock matrix with respect to the field, that contains both the above operators ($\Omega_k$ or $\vec{\nabla}_r$) and the bielectronic contribution through the perturbed density matrix (see Ref. [18]).

3. Results of the comparison

In the following, the SOS and CPHF (or CPKS) results obtained with the L and V operator for one molecular system, methane, and four crystalline systems, namely MgO, diamond, silicon and SiC, will be presented as a function of the adopted hamiltonian and basis set. A development version of the CRYSTAL code has been used [19]. CRYSTAL is a periodic ab initio program that adopts a gaussian type basis set. The experimental geometry is used in all cases. Standard values (6 6 6 6 12) are used for the parameters controlling the accuracy in evaluating Coulomb and Hartree-Fock exchange series [19]. The reciprocal space was sampled according to a regular sub-lattice with a shrinking factor IS equal to 10, that provides well converged results with both operators.

The SCF convergence threshold on the total energy (TE) is set to $10^{-7}$ Hartree, that ensures well converged results [4]. HF and DFT (in its LDA, GGA and B3LYP variants) levels of theory have been used.

3.1. Molecular case

Table 1 compares the polarizability of methane obtained with the L and V operators, by using the four different hamiltonians and three basis sets of increasing size. The two sets of data refer to the results obtained at the SOS and CPHF or CPKS levels; the former are simply the results at the first cycle of the Self-Consistent process performed to converge the latter.

| Method | Operator | STO-3G | DZP* | 6-311**(3d,3p) |
|--------|----------|--------|------|----------------|
| HF     | V        | 1.12   | 4.34 | 5.43           |
|        | L        | 5.65   | 13.54| 15.84          |
| B3LYP  | V        | 2.43   | 10.54| 12.65          |
|        | L        | 5.55   | 14.29| 16.73          |
| GGA    | V        | 3.15   | 14.92| 17.48          |
|        | L        | 5.54   | 15.15| 17.67          |
| LDA    | V        | 3.00   | 14.45| 17.26          |
|        | L        | 5.34   | 14.76| 17.41          |

The table shows that at the LDA and GGA levels the V and L results are quite different when the minimal STO-3G basis set is used (nearly 50% difference); when however a richer basis set is adopted, the difference reduces to 0.2 (GGA) or 0.15 (LDA) Bohr$^3$. The HF and B3LYP data, as expected, differ by as much as a factor 4 (HF) or 2 (B3LYP) at the minimal basis set level; a better basis set reduces the difference, as one of the two conditions mentioned above for the equivalence is better satisfied, but never eliminates it, as the other condition (non-commutability) still remains. The table then shows that, at least for pure DFT schemes,
the two operators can be used alternatively. In the molecular context, however, there is no computational or formal reason for using the $V \left( \nabla_r \right)$ operator, in the description of a static electric field perturbation, instead of the simpler to implement $L$ operator ($\vec{r}$). The situation is however slightly different for periodic systems, as we are going to show now.

3.2. Periodic case

For cubic systems, as the ones investigated here, the second order polarizability tensor is diagonal, with $\alpha = \alpha_{xx} = \alpha_{yy} = \alpha_{zz}$. The optical dielectric constant $\epsilon_\infty$ is related to $\alpha$ by the equation: $\epsilon_\infty = 1 + 4\pi\alpha/V$ where $V$ is the volume of the unit cell [21].

Table 2 shows the results of a preliminary study of the basis set effect on the $\epsilon_\infty$ values obtained with the $L$ and $V$ operators, in order to assess the minimal basis set size required for obtaining very close results from the two operators. It turns out that convergence is slow, and that the second set of polarization $d$ functions (the exponents of the $d$ shells are 1.75 and 0.4 Bohr$^{-2}$ for Mg and 1.10 and 0.19 Bohr$^{-2}$ for oxygen) still changes $\epsilon_\infty$ by about 25%, whereas the addition of a $f$ shell (with exponent 0.6 Bohr$^{-2}$) changes $\epsilon_\infty$ only on the third decimal figure, not reported in Table 2.

**Table 2.** Effect of the basis sets of Mg and O (Mg/O) on the LDA dielectric constant value of MgO. SOS values are in parentheses. The experimental lattice parameter has been used ($a=4.21 \text{ Å}$). The exponents of the most diffuse single gaussian $sp$ shells are 0.69, 0.30 (Mg) and 0.5, 0.185 (O) Bohr$^{-2}$ (d exponents are given in the text). The shrinking factor IS is 12.

| Operator | 8-511/8-411 | 8-511*/8-411 | 8-511*/8-411* | 8-511***/8-411** |
|----------|-------------|-------------|--------------|-----------------|
| $V$      | 1.97 (2.02) | 2.03 (2.06) | 2.44 (2.50)  | 3.17 (3.27)     |
| $L$      | 2.35 (2.40) | 2.43 (2.48) | 2.74 (2.83)  | 3.19 (3.29)     |

Basis sets of the same quality as the richest one used in Table 2 have been adopted also for Diamond, Silicon and SiC. The results for the four systems are reported in Table 3, where also the experimental data are given for comparison.

At the HF level of calculation, the obtained dielectric constant (SOS or CPHF) is much smaller than the experimental value. This is related to the too large band gap and to the dependence of $\alpha$ (then $\epsilon_\infty$) on $(\epsilon_{i,k} - \epsilon_{j,k})^{-1}$ and $(\epsilon_{i,k} - \epsilon_{j,k})^{-3}$ according to the use of $\Omega_k$ or $\nabla_r$ operators in the transition moment calculation. When the relaxation of the orbitals is taken into account in the SCF-CPHF process, a very large variation of $\epsilon_\infty$ is obtained in the direction of the experimental results (it increases by 30% for MgO, and by almost a factor 2 for Si). The $L$ value underestimates the experiment by something in between 20% (MgO, C) and 50% (Si), according to the band gap of the system. For $V$, the error due to the non commutability of $\vec{r}$ and $H_0$ (see previous section) adds to the band-gap error, so that the final value is very far from the experiment.

The DFT direct gap is too small, the best value being obtained with the B3LYP functional. The resulting $L$ dielectric constants are very close to experiment, except for silicon whose band-gap is very small, and for which the optical dielectric constant is very sensitive to the field-frequency. LDA and GGA provide too large SOS results, as a consequence of the too small band-gap. The SCF-CPKS scheme improves the results: the dielectric values decrease towards the experimental value. The table shows that the SCF process corrects in general the SOS results, increasing the HF values and decreasing the LDA or GGA values. LDA and GGA satisfy the commutation requirement for the equivalence of the $L$ and $V$ operators; this is clearly shown in the table, where the two results differ by less than 2% for the four systems.
Table 3. CPHF(KS) and SOS (in parentheses) dielectric constant of the diamond, SiC and Si evaluated at the experimental geometry (a = 3.56, 4.40 and 5.43 Å). Basis set: 6-21** (sp: 0.225; d: 1.5; 0.65 Bohr$^{-2}$) for C and 8-8411** (sp: 0.31; 0.145; d: 1.2; 0.3 Bohr$^{-2}$) for Si. IS=12. The direct gap is given in eV.

| Method | Property | Operator | MgO | C     | SiC   | Si     |
|--------|----------|----------|-----|-------|-------|-------|
|        | gap      | V        | 5.6 | 1.56  | 2.45  | 2.28  |
|        |          | L        | 2.9 | 2.49  | 5.04  | 5.07  |
|        |          | V        | 6.2 | 4.80  | 4.80  | 7.11  |
|        |          | L        | 7.3 | 7.3   | 6.2   | 7.71  |
| B3LYP  | $\epsilon^\infty$ | V        | 5.5 | 3.05  | 3.07  | 5.88  |
|        |          | L        | 5.6 | 5.65  | 5.73  | 4.5   |
| GGA    | $\epsilon^\infty$ | V        | 5.8 | 4.80  | 4.80  | 2.7   |
|        |          | L        | 5.8 | 5.73  | 5.73  | 4.5   |
| LDA    | $\epsilon^\infty$ | V        | 4.5 | 3.17  | 3.17  | 4.5   |
|        |          | L        | 4.5 | 5.80  | 5.80  | 4.5   |
| Exp.   | $\epsilon^\infty$ static (\(\lambda \rightarrow \infty\)) | from \(n = \sqrt{\epsilon}\) | 5.7$^a$ | 5.7$^a$ | 6.32$^c$ | 11.8$^c$ |

\(\lambda = 656\) nm (\(\lambda = 633\) nm) (\(\lambda = 633\) nm)

a: Ref. [22]; b: Ref. [23]; c: Ref. [24]; d: Ref. [25]

4. Conclusions

Two alternative strategies have been developed for the calculation of the dielectric tensor of crystalline compounds, that for brevity have been indicated as L and V. The L scheme requires the evaluation of the gradient with respect to the \(\vec{k}\) vectors of the crystalline orbitals at the various level of perturbation, which implies a certain degree of difficulty in the implementation of efficient computational schemes. The alternative V strategy requires the evaluation of gradients of the same crystalline orbitals with respect to the space variable, with a lower degree of difficulty and similar CPU time. The two formulations are however equivalent only when the exchange-correlation potential commutes with the position operator. Hartree-Fock and hybrid functionals cannot then exploit this equivalence without correcting for the non-commutability, and this reduces the interest for the V strategy.

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