High-order density-matrix perturbation theory

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We present a simple formalism for the calculation of the derivatives of the electronic density matrix $\rho$ at any order, within density functional theory. Our approach, contrary to previous ones, is not based on the perturbative expansion of the Kohn-Sham wavefunctions. It has the following advantages: (i) it allows a simple derivation for the expression for the high order derivatives of $\rho$; (ii) in extended insulators, the treatment of uniform-electric-field perturbations and of the polarization derivatives is straightforward.

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I. INTRODUCTION

Linear response methods\textsuperscript{1,2} within the density functional theory approach (DFT)\textsuperscript{3} have been successfully applied to compute a wide range of properties in real materials such as phonon dispersions, dielectric constants, effective charges,\textsuperscript{4} and NMR spectra.\textsuperscript{5}

Beyond linear response, perturbation theory applied to the Kohn-Sham (KS) orbitals allows the calculation of the derivatives of the energy at any order.\textsuperscript{6} This kind of approach has two disadvantages: (i) although the final result is gauge invariant, \textit{i.e.} invariant with respect to an arbitrary unitary rotation in the space of the occupied KS-orbitals,\textsuperscript{7} the formulation of the theory depends on the chosen gauge. This becomes apparent in the application of the KS-orbitals orthonormality constraints at high order. (ii) In the case of periodic systems, the treatment of a perturbation due to a uniform electric field is not trivial, because the position operator, necessary to describe such a perturbation, is ill-defined in periodic boundary conditions. Much effort has been devoted throughout the years to overcome this last problem. Early treatments of the electric field perturbation for the calculation of the second and third order susceptibilities are particularly complex.\textsuperscript{8} A simpler formalism for the calculation of the second order susceptibility was obtained in Ref.\textsuperscript{9} taking advantage of the $2n + 1$ theorem and of a Wannier representation of the orbitals. Only very recently Nuñes and Gonze\textsuperscript{10} were able to give an expression for the derivatives of the DFT energy, with respect to uniform electric fields, at any order, by introducing in the Hamiltonian an additional term depending on the polarization Berry phase.\textsuperscript{11}

We remark that, although a perturbation due to a macroscopic uniform electric field is ill-defined on an individual Bloch states, such a perturbation is well defined on individual Wannier states\textsuperscript{12,13} which can be obtained by a different choice of gauge. This consideration suggests that the two problems, mentioned in the previous paragraph, are related, and that both problems might possibly disappear using a perturbative approach which is \textit{not} based on the perturbative series of the single KS orbitals, but is solely based on the properties of the electronic density matrix $\rho$, which is a gauge independent operator. In a recent paper\textsuperscript{14} we gave an expression for the second order derivative of $\rho$ which allowed the efficient computation of Raman spectra.\textsuperscript{15} In the present paper we derive a general expression for the $n$-th order derivative of $\rho$, using the two relations $\rho^2 = \rho$, and $[\rho, H] = 0$, being $[,]$ a commutator and $H$ the KS Hamiltonian. To fix our notation we define the electronic density matrix as

$$\rho = \sum_v |\psi_v\rangle \langle \psi_v|,$$

where, throughout the paper, $v$ or $v'$ is an index running on the occupied valence states, and $|\psi_v\rangle$ are normalized KS-eigenstates, \textit{i.e.} $H|\psi_v\rangle = \epsilon_v |\psi_v\rangle$. Given a perturbation associated with a small parameter $\lambda$, for a generic quantity $F$, we consider the perturbation series:

$$F(\lambda) = F^{(0)} + \lambda F^{(1)} + \lambda^2 F^{(2)} + \lambda^3 F^{(3)} + \ldots \quad (1)$$

The generalization to the case of different perturbations $\lambda_1, \ldots \lambda_n$ is straightforward. $\rho$ and $H$ stand for $\rho(\lambda)$ and $H(\lambda)$. We call $P_V$ and $P_C$, respectively, the projectors on valence and conduction band states, \textit{i.e.} $P_V = \rho^{(0)} P_C = 1 - \rho^{(0)}$. Given an Hermitian operator $A$ we define $A_{CC} = P_C A P_C$, $A_{VV} = P_V A P_V$, $A_{CV} = P_C A P_V$, and $A_{VC} = (A_{CV})^\dagger$.

The work is organized as follows. In Sec. II we use the relation $\rho^2 = \rho$ to express $\rho^{(n)}$ as a function of the operators $\rho^{(i)}_{CV}$, having $i \leq n$. In Sec. III we use the relation $[H, \rho] = 0$ to obtain an expression for $\rho^{(n)}_{CV}$ that can be easily computed using standard linear response techniques. In Sec. IV we show that, within our formalism, the perturbations due to a uniform electric field are well defined in extended insulators. In Sec. V we derive a simple expression for the derivatives of the polarization.

II. $\rho^{(n)}$ AS A FUNCTION OF $\{\rho^{(i)}_{CV}\}$, WITH $i \leq n$

We decompose $\rho$ in $\rho_{CC} + \rho_{VV} + \rho_{CV} + \rho_{VC}$, and we consider these four terms separately. The idempotency condition, $\rho^2 = \rho$, implies that $P_C \rho P_C = P_C \rho P_C = \rho_{CC}$, $P_V \rho P_V = P_V \rho P_V = \rho_{VV}$, $P_C \rho P_V = P_C \rho P_V = \rho_{CV}$, $P_V \rho P_C = P_V \rho P_C = \rho_{VC}$.
\( P_C \rho (P_C + P_V) \rho P_C, \) or
\[
\rho_{CC} - \rho_{CC} \rho_{CC} = \rho_{CV} \rho_{VC}.
\]
When all the eigenvalues of \( \rho_{CC} \) are lower than 1/2, i.e., for \( \lambda \) sufficiently small, this relation between the two operators \( \rho_{CC} \) and \( \rho_{CV} \rho_{VC} \) can be inverted to obtain:
\[
\rho_{CC} = \frac{1 - \sqrt{1 - 4 \rho_{CV} \rho_{VC}}}{2}, \quad (2)
\]
where the right-hand side denotes the operator obtained substituting \( \rho_{CV} \rho_{VC} \) in the Taylor series
\[
\frac{1 - \sqrt{1 - 4x}}{2} = x + x^2 + 2x^3 + 3x^4 + \ldots \quad (3)
\]
In a similar way, defining \( \Delta \rho_{VV} = \rho_{VV} - \rho^{(0)} \),
\[
\Delta \rho_{VV} \Delta \rho_{VV} + \Delta \rho_{VV} = \rho_{VV} \rho_{VV} - \rho_{VV} = -\rho_{CV} \rho_{CV}.
\]
When all the eigenvalues of \( \Delta \rho_{VV} \) are larger than \(-1/2 \), i.e., for \( \lambda \) sufficiently small, \( \Delta \rho_{VV} \) can be expressed as a function of \( \rho_{CV} \rho_{VC} \):
\[
\Delta \rho_{VV} = \rho_{VV} - \rho^{(0)} = -\frac{1 - \sqrt{1 - 4 \rho_{CV} \rho_{VC}}}{2}. \quad (4)
\]
Finally, \( \rho^{(n)} \) can be expressed as a function of the \( \{ \rho_{CV}^{(i)} \} \), with \( i \leq n \), using the relation
\[
\rho^{(n)} = \rho_{CV}^{(n)} + \rho_{VC}^{(n)} + \rho_{PC}^{(n)} + \rho_{VV}^{(n)}, \quad (5)
\]
and taking the \( n \)-th order variation of Eq. (2) and Eq. (4) through Eq. (6). As examples, observing that \( \rho_{CV}^{(0)} = 0 \), is easy to show that
\[
\rho^{(1)} = \rho_{CV}^{(1)} + \rho_{VC}^{(1)}, \quad (6)
\]
\[
\rho^{(2)} = \rho_{CV}^{(2)} + \rho_{VC}^{(2)} + [\rho_{CV}^{(1)}, \rho_{VC}^{(1)}], \quad (7)
\]
\[
\rho^{(3)} = \rho_{CV}^{(3)} + \rho_{VC}^{(3)} + [\rho_{CV}^{(2)}, \rho_{VC}^{(2)}] + [\rho_{CV}^{(1)}, \rho_{VC}^{(1)}], \quad (8)
\]
\[
\rho^{(4)} = \rho_{CV}^{(4)} + \rho_{VC}^{(4)} + [\rho_{CV}^{(3)}, \rho_{VC}^{(3)}] + [\rho_{CV}^{(2)}, \rho_{VC}^{(2)}] + [\rho_{CV}^{(1)}, \rho_{VC}^{(1)}] + [\rho_{CV}^{(1)} \rho_{CV}^{(1)}] + [\rho_{CV}^{(1)} \rho_{CV}^{(1)}]. \quad (9)
\]
Note that each \( \rho_{CV}^{(i)} \) is a gauge independent operator.

In Eqs. (6-9), \( \rho^{(n)} \) is expressed as \( \rho_{CV}^{(n)} + \rho_{VC}^{(n)} \) plus a commutator, for \( n \leq 4 \). This property is used in Sec. IV to compute the derivatives of the polarization. It holds at any order \( n \). Indeed, as we show in the appendix:
\[
\rho^{(n)} = \rho_{CV}^{(n)} + \rho_{VC}^{(n)} + \sum_{i=1}^{n-1} \rho_{CV}^{(i)} \rho_{VC}^{(n-i)} = \rho_{CV}^{(n)} + \rho_{VC}^{(n)} + \sum_{i=1}^{n-1} \rho_{CV}^{(i)} \rho_{VC}^{(n-i)}, \quad (10)
\]
where \( n \geq 2 \), and
\[
O_{VC} = \rho_{VC} \frac{1 - \sqrt{1 - 4 \rho_{CV} \rho_{VC}}}{2 \rho_{CV} \rho_{VC}} = \frac{1 - \sqrt{1 - 4 \rho_{CV} \rho_{VC}}}{2 \rho_{CV} \rho_{VC}} \rho_{CV} \quad (11)
\]

III. COMPUTATION OF \( \rho_{CV}^{(n)} \)

In order to compute \( \rho_{CV}^{(n)} \) we introduce the wavefunction \( |\eta_v^{(n)}\rangle = P_C |\psi_v^{(n)}\rangle \), \( |\psi_v^{(0)}\rangle \) being an unperturbed KS eigenvector. We have:
\[
\rho_{CV}^{(n)} = \sum_{v} P_C |\psi_v^{(0)}\rangle \langle \psi_v^{(0)}| \langle \eta_v^{(n)}| \langle \eta_v^{(n)}| = \sum_{v} |\eta_v^{(n)}\rangle \langle \eta_v^{(n)}|. \quad (12)
\]
Equating to zero the \( n \)-th order term of the perturbation series of \( [H, \rho] = 0 \), we find:
\[
\sum_{i=0}^{n} [H^{(i)}, \rho^{(n-i)}] = 0.
\]
Multiplying this relation on the left by \( P_C \) and applying to \( |\psi_v^{(0)}\rangle \) to the right, we derive:
\[
[H^{(0)} - \epsilon_v^{(0)}] |\eta_v^{(n)}\rangle = - \sum_{i=1}^{n} P_C [H^{(i)}, \rho^{(n-i)}] |\psi_v^{(0)}\rangle. \quad (13)
\]
Solving the linear system of Eq. (13) one can obtain \( |\eta_v^{(n)}\rangle \) and, thus, \( \rho^{(n)} \). Since the right-hand side of Eq. (13) depends on \( H^{(n)} \), that in turn depends on \( \rho^{(n)} \), the system is to be solved self-consistently, \( \eta_v^{(n)} \) being an unperturbed KS eigenvector. Thus Eqs. (10) and (11) give an efficient algorithm that can be easily implemented in available DFPT codes (as the PWSCF code), to compute the derivatives of \( \rho \) at any order.

Alternatively, Eq. (13) can be written as
\[
|\eta_v^{(n)}\rangle = \tilde{G}_v \left( \sum_{i=1}^{n} [H^{(i)}, \rho^{(n-i)}] \right) |\psi_v^{(0)}\rangle, \quad (14)
\]
where \( \tilde{G}_v = \sum_{\nu} |\psi_v^{(0)}\rangle \langle \psi_v^{(0)}| / (\epsilon_v^{(0)} - \epsilon_{\nu}) \) is the unperturbed Green function operator projected on the conduction band, and the sum \( \sum_\nu \) is restricted to the empty conduction-band states. From Eq. (14) one can recognize that \( |\eta_v^{(1)}\rangle = P_C |\psi_v^{(1)}\rangle \) and that \( |\eta_v^{(2)}\rangle \) is the projection on the conduction band of the KS orbital \( \psi_v \) in the parallel-transport gauge of Ref. 5. However, at higher orders, there is not such a simple relation between the \( |\eta_v^{(n)}\rangle \) functions, defined in the present paper, and the variations of the KS orbitals.

Finally, as examples, we write \( \rho^{(1)} \) as a function of the
\(|\eta^{(i)}_{\alpha}\rangle\) wavefunctions, for the three lowest order:

\[
\rho^{(1)} = \sum_v \left( |\eta^{(1)}_v\rangle \langle \psi^{(0)}_v| + |\psi^{(0)}_v\rangle \langle \eta^{(1)}_v| \right) \tag{15}
\]

\[
\rho^{(2)} = \sum_v \left( |\eta^{(2)}_v\rangle \langle \psi^{(0)}_v| + |\psi^{(0)}_v\rangle \langle \eta^{(2)}_v| + |\eta^{(1)}_v\rangle \langle \eta^{(1)}_v| \right) + \\
- \sum_{v,v'} |\psi^{(0)}_v\rangle \langle \eta^{(1)}_{v'}| \langle \psi^{(0)}_{v'}| \tag{16}
\]

\[
\rho^{(3)} = \left( \sum_v |\psi^{(0)}_v\rangle \langle \eta^{(2)}_v| + \sum_v |\eta^{(2)}_v\rangle \langle \eta^{(1)}_v| + \\
- \sum_{v,v'} |\psi^{(0)}_v\rangle \langle \eta^{(2)}_{v'}| \langle \psi^{(0)}_{v'}| \right) + (\ldots)\dagger. \tag{17}
\]

We already used Eq. (16) in Ref. 11, to compute the Raman tensor.

**IV. TREATMENT OF THE ELECTRIC FIELDS**

Thanks to the commutators in Eq. (13), all the quantities needed to compute \(\rho^{(n)}\) are well defined in an extended insulator, even if the perturbation \(\lambda\) is the component \(E_{\alpha}\) of a uniform electric field, i.e., if \(H^{(1)} = -e\alpha \cdot \partial V_{\text{Hxc}} / \partial E_{\alpha}\) being \(\alpha\) the \(\alpha^{th}\) Cartesian component of the position operator \(r\), \(e\) the electron charge, and \(V_{\text{Hxc}}\) the Hartree and exchange-correlation potential. In particular, in an insulator, the commutator \([r, \rho^{(n-1)}]\) which appears in Eq. (13), is a well-defined bounded operator, since the variation of the density matrix is localized \((r''|\rho^{(n-1)}|r')\) goes to zero exponentially for \(|r'' - r'| \to \infty\).

To prove the localized nature of \(\rho^{(n-1)}\) in a periodic system, we notice that \(\rho^{(n-1)}\) can be written (see Eq. (18)) as a sum of operators of the type

\[
D = \sum_{k\nu} |\alpha_{k\nu}\rangle \langle \beta_{k\nu}|,
\]

where \(|\alpha_{k\nu}\rangle\) and \(|\beta_{k\nu}\rangle\) are Bloch wavefunction, i.e., \(|\alpha_{k\nu}\rangle = e^{ik\boldsymbol{r}} |\tilde{\alpha}_{k\nu}\rangle / \sqrt{N}\) and \(|\beta_{k\nu}\rangle = e^{ik\boldsymbol{r}} |\tilde{\beta}_{k\nu}\rangle / \sqrt{N}\), being \(N\) the number of unit cells, \(|\tilde{\alpha}_{k\nu}\rangle\) and \(|\tilde{\beta}_{k\nu}\rangle\) wavefunctions periodic in the lattice, normalized on the unit cell. In an insulator, the operators

\[
D_k = \sum_{\nu} |\alpha_{k\nu}\rangle \langle \beta_{k\nu}|
\]

are analytic in \(k\) and periodic in the reciprocal space. Cloizeaux has shown in Ref. 10 that an operator having the properties of \(D\) is exponentially localized.

The representation of \(\rho^{(n-1)}\) in terms of \(D\) is also useful to obtain a practical expression for the calculation of the \([r, \rho^{(n-1)}]\) commutator. In the limit of a converged \(k\)-points grid,

\[
\frac{1}{N} \sum_k \frac{\partial}{\partial k_{\alpha}} D_k = \Omega_c \int \frac{d^3 k}{(2\pi)^3} \frac{\partial}{\partial k_{\alpha}} D_k = 0,
\]

since the integral over its period of the derivative of a periodic analytic function is zero. \(\Omega_c\) is the unit-cell volume. From this it can be easily demonstrated that

\[
[r_{\alpha}, D] = \frac{i}{N} \sum_{k\nu} e^{ik\boldsymbol{r}} \frac{\partial |\tilde{\alpha}_{k\nu}\rangle \langle \tilde{\beta}_{k\nu}|}{\partial k_{\alpha}} e^{-ik\boldsymbol{r}}. \tag{18}
\]

The terms required in Eq. (13), when the perturbation is a uniform electric field, can thus be computed using

\[
\langle \psi^{(0)}_{k\nu} | [r_{\alpha}, D] | \psi^{(0)}_{k\nu} \rangle = \frac{i}{N} \sum_{\nu'} \langle \tilde{\psi}^{(0)}_{k\nu} \rangle \frac{\partial |\tilde{\alpha}_{k\nu'}\rangle \langle \tilde{\beta}_{k\nu'}|}{\partial k_{\alpha}} \langle \tilde{\psi}^{(0)}_{k\nu'} \rangle, \tag{19}
\]

where \(|\tilde{\psi}^{(0)}_{k\nu}\rangle\) are the periodic part of the Bloch wavefunctions, i.e., \(|\tilde{\psi}^{(0)}_{k\nu}\rangle = e^{ik\boldsymbol{r}} |\tilde{\psi}^{(0)}_{k\nu}\rangle / \sqrt{N}\), and the bra-ket products on the right-hand side are performed on the unit cell. In practical implementation, the derivative with respect to \(k_{\alpha}\) in the right-hand side of Eq. (19) can be computed numerically by finite-differentiation, using an expression independent from the arbitrary wavefunction-phase, as in Refs. 11, 13.

**V. DERIVATIVES OF THE POLARIZATION**

Finally, with the present formalism, the computation of the \(n\)-th order variation of the polarization density \(P^{(n)}\) becomes natural. The components of \(P^{(n)}\) can be written as:

\[
P^{(n)}_{\alpha} = -\frac{2e}{N\Omega_c} Tr \{ r_{\alpha} \rho^{(n)} \}, \tag{20}
\]

where the factor two accounts for the spin degeneracy and \(Tr\{A\}\) is the trace of the operator \(A\). We substitute \(\rho^{(n)}\) from Eq. (10) into Eq. (20). Using the trace property \(Tr\{[A, B]C\} = Tr\{A[B, C]\}\), it is easy to arrive at:

\[
P^{(n)}_{\alpha} = -\frac{2e}{N\Omega_c} \sum_{k\nu\nu'} Tr \left( \langle \tilde{\psi}^{(0)}_{k\nu} \rangle \frac{\partial |\tilde{\psi}^{(0)}_{k\nu'}\rangle \langle \tilde{\psi}^{(0)}_{k\nu'}|}{\partial k_{\alpha}} \psi^{(0)}_{k\nu} \rangle + \sum_{i=1}^{n-1} \langle \chi^{(n-1)}_{k\nu} \rangle \frac{\partial |\tilde{\psi}^{(0)}_{k\nu'}\rangle \langle \tilde{\psi}^{(0)}_{k\nu'}|}{\partial k_{\alpha}} \psi^{(0)}_{k\nu} \rangle \right), \tag{21}
\]
where \( n \geq 2 \), \( \text{Im}(z) \) is the imaginary part of the complex number \( z \), and we have written the operators \( O_{\nu}^{(i)} \) as
\[
O_{\nu}^{(i)} = \sum_{k} |\psi_{\nu k}^{(0)}\rangle\langle\chi_{\nu k}^{(i)}|,
\]
being \( |\chi_{\nu k}^{(i)}\rangle = O_{CV}^{(i)}|\psi_{\nu k}^{(0)}\rangle \).

VI. CONCLUSIONS

Concluding, we presented a formalism for the calculation of the derivatives of the electronic density matrix at any order, within the density functional theory approach. Beside being simple, this formalism allows the treatment of extended systems in the presence of an external uniform electric fields in a natural way, without introducing in the Hamiltonian an additional term depending on the polarization Berry-phase.

APPENDIX

The operators defined in Eq. (11) are well defined for \( \lambda \) sufficiently small, since the series
\[
1 - \sqrt{1 - 4x} = 1 + x + 2x^2 + 5x^3 + \ldots
\]
has the same convergence properties of Eq. (9). From Eq. (11) of the text, \( \rho_{CC} = \rho_{CV} O_{VC} = O_{CV} \rho_{VC} \) and \( \rho_{VV} = -\rho_{(0)} + O_{CV} \rho_{VC} = -\rho_{CV} O_{VC} \). For \( n \geq 2 \) the \( n \)-th order variation of \( \rho_{CC} \) and \( \rho_{VV} \) are:
\[
\rho_{VV}^{(n)} = -\sum_{i=1}^{n} O_{CV}^{(n-i)} \rho_{VC}^{(i)} = -\sum_{i=1}^{n} \rho_{VC}^{(n-i)} O_{CV}^{(i)}.
\]

Eq. (10) of the text easily follows.

Writing \( O_{CV}^{(n)} \) as a function of \( \rho_{CV}^{(i)} \), at the lowest orders we have:
\[
O_{VC}^{(1)} = \rho_{VC}^{(1)}
\]
\[
O_{VC}^{(2)} = \rho_{VC}^{(2)}
\]
\[
O_{VC}^{(3)} = \rho_{VC}^{(3)} + \rho_{CV}^{(1)} \rho_{CV}^{(1)} \rho_{VC}^{(1)}
\]
\[
O_{VC}^{(4)} = \rho_{VC}^{(4)} + \sum_{i,j,k} \rho_{CV}^{(i)} \rho_{CV}^{(j)} \rho_{CV}^{(k)} \delta_{i+j+k,4}
\]
\[
O_{VC}^{(5)} = \rho_{VC}^{(5)} + \sum_{i,j,k} \rho_{CV}^{(i)} \rho_{CV}^{(j)} \rho_{CV}^{(k)} \delta_{i+j+k,5}
\]
\[
+ 2 \rho_{VC}^{(1)} \rho_{CV}^{(1)} \rho_{CV}^{(1)} \rho_{CV}^{(1)} \rho_{CV}^{(1)}
\]
where \( \sum^{*} \) is a sum on positive integers. These equations allows to compute \( \rho^{(n)} \), with \( n \leq 6 \).

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