Orbital-unrelaxed Lagrangian density matrices for periodic systems at the local MP2 level

Denis Usvyat and Martin Schütz
Institute of Physical and Theoretical Chemistry, University of Regensburg, Universitätsstraße 31, D-93040 Regensburg, Germany
E-mail: denis.usvyat@chemie.uni-regensburg.de, martin.schuetz@chemie.uni-regensburg.de

Abstract. In the present paper a method based on the Hylleraas functional is proposed in order to obtain correlated ground state density matrices for periodic systems at the level of local MP2. The general properties of these density matrices, namely size-extensivity, translational invariance, exponential decay of the off-diagonal elements, etc are discussed. As test examples we investigate the influence of the electron correlation on the density in diamond and strontium titanate (in the latter case via the Mulliken charges). The calculations reveal that in diamond the concentration of the electrons in the bond region decreases when the correlation is taken into account, but the change in the density relative to Hartree-Fock is small. In the case of SrTiO$_3$, this change is more significant and causes a lowering of the ionicity of this crystal.

1. Introduction

During the last two decades several approaches, which allow to adapt molecular quantum chemical methods to periodic systems have been proposed. Among those focusing on the ground state are the canonical correlation methods for one-dimensional systems (polymers) [1, 2, 3, 4], the local Anzatz by Stollhof and Fulde [5, 6, 7], Stolls’s incremental scheme [8, 9, 10] (successfully applied to various systems by Paulus and co-workers [11, 12, 13, 14]), Almlöf’s Laplace-transform technique [15] reformulated for periodic MP2 case by Ayala et al. [16], and the periodic local MP2 (LMP2) method of the CRYSCOR project [17, 18, 19].

All the above approaches aim at correlated level calculations of the total ground state energy of periodic systems, equilibrium geometries (both the lattice parameters and the atomic arrangements within the unit cell), elastic properties, vibrational frequencies, cohesion energies etc. At the same time, the response of the system to an external perturbation, which is described to first order by the first order properties, is also a topic of interest in quantum chemistry. In molecules the simplest property of such a kind is the electric dipole moment. For variational methods the Hellmann-Feynman theorem ensures that the first order properties can equivalently be evaluated as the first derivatives of the energy w.r. to the related field strengths and as the expectation values over the related perturbation operator. In non-variational methods like Coupled Cluster or MP2 theory these two approaches are not equivalent and the former is clearly preferable.

In periodic systems a dipole moment is ill-defined, since the position vector operator is not consistent with the translational symmetry [20]. However, the density matrices are still of a great importance since they allow to evaluate experimentally observable quantities such as the electron
density, Compton profiles, etc. In HF or DFT methods, which are the common computational tools in the solid state physics, the density matrix (or the density) is an essential ingredient of the formalism and thus is obtained automatically. Yet for periodic correlated methods a proper definition of the density matrix is not so straight-forward.

In a number of cases (e.g., weakly bound systems) neither HF nor the standard DFT approaches provide sufficiently reliable results. Therefore it is desirable to include electron correlation in the calculations. In the last several years Professor Pisani has been working very actively and effectively in this direction. In the framework of the periodic LMP2 method Pisani et al. have proposed a formalism for calculating the periodic LMP2 density matrix based on a direct utilization of the LMP2 wavefunction [21, 22]. In order to deal with the non-size-extensivity of the MP2 wavefunction, which is indeed harmful in case of an infinite system like a crystal, additional approximations have been introduced, consisting mainly of the restriction of one of the summation indices to the reference cell and a subsequent adaptation of the so obtained density matrix to the translational symmetry.

In this article we propose an alternative approach to the periodic LMP2 density matrix, which we define as a formal density matrix corresponding to the evaluation of first-order properties as the first derivative of the orbital-unrelaxed LMP2 Lagrangian with respect to the strength of a perturbation. Since only the LMP2 energy rather than the wavefunction is involved in the formalism, this approach is size-consistent. Besides, it allows for further improvement by including the orbital relaxation (and localization) conditions in the Lagrangian.

The technique presented here can be applied to any periodic MP2 scheme. The platform used here is the periodic local MP2 method implemented in the CRYSCOR program [17, 18, 19], which builds upon periodic LCAO code CRYSTAL [23]. The latter offers the machinery to calculate numerous different properties relevant for periodic systems from the related (correlated) density matrices.

2. Theory
Our approach to the corresponding density matrices is formulated through the derivative of the LMP2 total energy, which is in its standard form non-variational. The standard way in Coupled Cluster theory (to which MP2 is an approximation correct to first order in the amplitudes) to deal with this problem is to set up a Lagrangian [24], which for MP2 takes the form

\[ L^{MP2} = \langle 0 | H + [H, T_2] | 0 \rangle + \sum_{\mu_2} \tilde{t}_{\mu_2} (\mu_2) | H + [F, T_2] | 0 \rangle. \]  

(1)

In eq. (1) \( H \) and \( F \) represent the Hamiltonian and Fock operator, respectively (which both may include an external perturbation due to a field), \( T_2 \) is the doubles excitation operator

\[ T_2 = \sum_{\mu_2} t_{\mu_2}^{(1)} \tau_{\mu_2} \]  

(2)

with amplitudes \( t_{\mu_2}^{(1)} \) correct to first order in the fluctuation potential, and \( | \mu_2 \rangle = \langle 0 | \tau_{\mu_2}^\dagger \) stands for the doubles projection manifold. The Lagrangian is required to be stationary w.r. to all wavefunction parameters, i.e., for the MP2 case the amplitudes \( t_{\mu_2}^{(1)} \) and multipliers \( \tilde{t}_{\mu_2} \). This leads immediately to equations which have to be fulfilled by these parameters. For MP2 it turns out that the multipliers \( \tilde{t}_{\mu_2} \) are identical to the (contravariant) amplitudes,

\[ \tilde{t}_{ij} = 2t_{ij} - t_{ji}, \]  

(3)

(which is valid also in the presence of an external perturbation). Using this condition in eq. (1) leads to the Hylleraas functional depending on only one independent set of wavefunction
parameters. The latter can be written in the form [25]

\[ E_2 = \sum_{ia,jb} ((ia|jb) + R_{ab}^{ij})(2t_{ab}^{ij} - t_{ba}^{ij}), \]  

(4)

where \( R_{ab}^{ij} \) is the MP2 residual

\[ R_{ab}^{ij} = (ia|jb) + \sum_c (f_{ac}t_{cb}^{ij} + t_{ac}^{ij}f_{cb}) - \sum_k (f_{ik}t_{kj}^{ab} + t_{ik}^{ab}f_{kj}), \]  

(5)

which becomes zero at convergence. Here we used the convention that the indices \( i, j, k, \ldots \) and \( a, b, c, \ldots \) denote the occupied and virtual orbitals, respectively, \( (ia|jb) \) is a electron-repulsion integral in chemical notation, and \( f \) stands for the Fock matrix. In the expression (5) the orbitals are assumed to be orthogonal.

Now we consider the external perturbation in \( H \) explicitly, i.e., \( H = H_0 + \alpha X \). The corresponding property then can be defined as the derivative of the energy w.r. to the perturbation strength \( \alpha \),

\[ \langle X \rangle = \left. \frac{dE_{MP2}}{d\alpha} \right|_{\alpha=0} = \left. \frac{dL_{MP2}}{d\alpha} \right|_{\alpha=0} = \left. \frac{\partial L_{MP2}}{\partial \alpha} \right|_{\alpha=0} \]

\[ = \langle 0|X|0 \rangle + \sum_{\mu_2} \bar{t}_{\mu_2} \langle \mu_2|X + [X, T_2]|0 \rangle \]

\[ = \langle 0|X|0 \rangle + \sum_{\mu_2} \bar{t}_{\mu_2} \langle \mu_2|[X, T_2]|0 \rangle \]  

(6)

Evaluating the second term in the eq. (6) (e.g. by means of the diagrammatic techniques [26, 27]) yields:

\[ \langle X \rangle = \langle 0|X|0 \rangle + 2 \sum_{ac} X_{ac} \sum_{ijb} \bar{t}_{ab}^{ij} + 2 \sum_{ki} X_{ki} \sum_{jab} \bar{t}_{ab}^{ij} k^{kj} \]  

(7)

This can be rewritten as the trace of matrix of the operator \( X \) with a formal density matrix \( D \) as

\[ \langle X \rangle = \langle 0|X|0 \rangle + \sum_{pq} X_{pq} D_{qp}, \]  

(8)

where the \( D \) is defined as

\[ D_{ij} = -2 \sum_{kab} \bar{t}_{ab}^{ij} k^{ik}, \]  

(9)

\[ D_{ab} = 2 \sum_{ijc} \bar{t}_{bc}^{ij} k^{ac}. \]  

(10)

The expressions (9) and (10) provide the MP2 correction to the HF density matrix.

Now we switch to the periodic local MP2 scheme [28, 17, 18, 19]. The occupied and virtual spaces are spanned by orthogonal localized orbitals (Wannier functions, WFs) and non-orthogonal projected atomic orbitals (PAOs), respectively. For orbital pairs \( (ij) \) the allowed PAOs (corresponding to a priori specified non-zero amplitudes) are confined to orbital pair-domains \( [ij] \) which comprise only PAOs being spatially close to the WF \( i \) or \( j \). Finally, in the periodic case any localized orbital is defined by a pair of indices (rather than one): the first
distinguishing between the orbitals in a reference cell and the second, for which we use the calligraphic font, defining the translation vector: \( j \rightarrow j, \mathcal{J} \), etc. Summing this up we rewrite the equations (9) and (10) within the periodic local MP2 formalism as

\[
D_{i,j,\mathcal{J}} = -2 \sum_{kK} \sum_{c',cD\in [kK]} \sum_{d',d'\in [jJ]} \overline{T}_{c'c}^{jKc} D_{i,kK}^{c} D_{i,kK}^{c'} D_{i,kK}^{c} D_{i,kK}^{c'} \sum_{d'd'\in [jJ]} S_{c'c}^{d'd'} S_{d'd'}^{d'd'}
\]

(11)

\[
D_{a,bB} = 2 \sum_{kKJL} \sum_{c',c\in [kKJL]} \overline{T}_{c'c}^{jKc} D_{a,kKJL}^{c} D_{a,kKJL}^{c'} D_{a,kKJL}^{c} D_{a,kKJL}^{c'} \sum_{d'd'\in [jJ]} S_{c'c}^{d'd'} S_{d'd'}^{d'd'}
\]

(12)

Here \( S \) stands for the PAO overlap matrix and the translational symmetry

\[
\overline{T}_{aA}^{bB} = \overline{T}_{aA}^{bB} \equiv S_{ab}^{B\oplus A}
\]

(13)

is exploited. The summation in (12) is performed over only those WFs \( kK \) and \( lL \) which contain the PAOs \( a \) and \( bB \) in their domain: \( a, bB \in [kKJL] \).

We wish to point out here that the MP2 Lagrangian (1) is not the complete Lagrangian describing the response of the system to an external perturbation. Additionally, the change in the Hartree-Fock reference and also in the localization of the orbitals has to be taken into account. This translates to adding the constraints of the Brillouin theorem condition and the localization extremum for the Wannier functions [29]. In fact, inclusion of the orbital relaxation effects in the definition of the density matrix for the MP2 method is more important than for Coupled Cluster approaches, since in the latter the orbital relaxation by virtue of Thouless theorem [30] is to a large extent covered by the singles part of the Lagrangian, which is not present in MP2 case. This issue is also discussed in Sec. 3. The orbital-relaxed implementation of the periodic LMP2 density matrix will be addressed in future work.

3. Discussion

Several points concerning the described method are worth discussing, also in comparison with the methods proposed in Refs. [21, 22].

(i) The density matrix obtained with the scheme proposed here is defined via the MP2 energy and the wavefunction is not involved. It is therefore size-extensive, which is of particular importance in the context of extended systems like solids.

(ii) The density matrices are translationally invariant:

\[
\begin{align*}
D_{i,j,\mathcal{J}} & = D_{i,j,\mathcal{J} \oplus \mathcal{I}} \\
D_{aA,bB} & = D_{a,b(B \oplus A)}
\end{align*}
\]

(14)

which is a consequence of the translational symmetry of the quantities involved in the expressions (11) and (12).

(iii) The density matrix values \( D_{a,bB} \) and \( D_{i,j,\mathcal{J}} \) decay exponentially with respect to the spatial separation between \( a \) and \( bB \) or \( i \) and \( j, \mathcal{J} \). For ease of analysis we refer to the equations (9) and (10). The doubles amplitudes \( t_{ab}^{ij} \) in the same manner as the integrals \( (ia|jb) \) decay exponentially with the distance between the functions \( i \) and \( a \) or \( j \) and \( b \). For the internal part of the density matrix (9) the amplitude \( t_{ab}^{jk} \) hence vanishes if the PAO \( a \) is far from WF \( i \). At the same time for non-vanishing amplitudes \( \overline{T}_{ab}^{jk} \) the PAO \( a \) should be close either to \( j \) or to \( k \). The former case ensures exponential decay of the density matrix either
through $t_{ab}^{ij}$ or $t_{ab}^{jk}$ with the distance between $i$ and $j$. In the latter case the amplitudes decay in the same way due to the separation between $k$ and either $a$ or $b$. A similar analysis reveals the exponential decay of also the external density matrix (10). The very same conclusions also follow for the periodic case with non-orthogonal PAOs, since the elements of the PAO overlap matrix appearing in (11) and (12) also decay exponentially with the distance between the related PAOs. Therefore the additional PAO overlap matrices do not affect the decay rate of the amplitude-overlap products.

(iv) There is no need to impose any additional approximation on the ranges of the summation indices in (11) and (12). We again base our analysis on equations (9) and (10). The amplitudes $t_{ab}^{ij}$ vanish (like the integrals) as $R^{-3}$ with the distance $R$ between $i$ and $j$, thus their products as $R^{-6}$. Consequently, if in (9) $i$ is close to $j$ and $a$ is close to both of them (otherwise the product of the amplitudes will vanish exponentially) the range of the index $k$ is governed by the $R^{-6}$ decay. The summations in (10) over $i$ or $j$ are as compact. Indeed, when the PAOs $a$ and $b$ are both spatially close to, say, WF $i$ and the PAO $c$ is close to $j$ the decay of the product of the amplitudes is again $R^{-6}$. In crystals (slabs) due to 3D (2D) packing the $R^{-6}$ decay reduces to $R^{-4}$ ($R^{-5}$), which is though slower than an exponential decay, but still makes the corresponding summations in (11) and (12) absolutely convergent. In our implementation the different terms, before being explicitly calculated, are prescreened by considering the product of the largest values of the amplitudes and overlaps involved.

(v) The Coupled Cluster density matrices are in general non-symmetrical. However, for the MP2 case, due to the simple form of the MP2 Lagrangian where the multipliers are identical to the contravariant amplitudes the MP2 density matrix is symmetrical:

$$D_{i,j}^{J} = D_{j,i}^{J}$$
$$D_{a,b}^{B} = D_{b,a}^{B}$$

(vi) The density matrices can be "improved" by including also orbital relaxation effects. For this purpose one has to augment the MP2 Lagrangian by the additional conditions for the orbitals. Equations for the related multipliers then again follow from the additional stationarity conditions the Lagrangian has to fulfill, which leads to the so called Z-CPHF (Coupled Perturbed Hartree Fock) and the Z-CPL (Coupled Perturbed Localization) equations [29]. For the latter one has to employ a well-defined single localization functional for the WFs, which is usually available for the case of molecules, but far less trivial for the case of crystals [31].

In the following we present results from test calculations for the diamond crystal, in which we investigated the alteration of the electron density obtained at the MP2 level relative to that of Hartree Fock. The Hartree Fock reference was calculated with the CRYSTAL code by using the 6-21G* basis set [32, 33]. The LMP2 amplitudes were evaluated employing the Density Fitting approximation as implemented in CRYSCOR [18, 19]. The MOLPRO Poisson triple-zeta-quality fitting basis set [34, 35] was utilized. The tolerances for the distant and very-distant pair cut-off distances were set to 4 and 8 Ångstrom, respectively. This implies that integrals up to an inter-orbital distance of 4 Ångstrom were calculated exactly, i.e., with the DF approximation, while integrals with an inter-orbital distance between 4 and 8 Ångstrom were obtained via Multipole approximation. Other integrals were neglected. The domains were chosen such that they cover the PAOs of 8 carbon atoms.

Fig.1 displays the contour plot of the LMP2-HF differential electron density in the (110) plane. Evidently, the LMP2 result correctly exhibits the trend of reducing the electronic density in the bonding region due to electron correlation (electrons can avoid each other more efficiently
than in a pure mean field approximation). However the absolute values of the differential density are two orders of magnitude smaller that those of the HF density itself, implying that the MP2 correction to the density is hardly noticeable at the absolute density scale.

In order to investigate whether such a small change in the density is a result of the lack of orbital relaxation effects in our approach we performed a calculation of the MP2 correction to the HF density (at the cc-pVDZ level) for a simple ethane molecule, which also possesses a single C-C bond. We used the MOLPRO code [36] for that purpose, which includes orbital relaxation in the MP2 density matrix. The 3D plot of this correction is given in Fig.2. The picture is similar to that of diamond – the differential density is negative in the bond region. The value for the contour of 0.005 Bohr$^{-3}$ shows that the correction to the density is still very small at the the scale of the density itself. At the same time it is a bit larger than that of the diamond, probably due to inclusion of the orbital relaxation effects.

In addition we studied another system where the inclusion of electron correlation causes a more pronounced change in the density – an incipient ferroelectric SrTiO$_3$ crystal [37]. The bonding in this crystal is of mixed covalent-ionic character. The Mulliken charges are considered as a measure for the ionicity of the system [38]. The cubic perovskite phase of this crystal with a lattice constant of 3.905 Å was taken. We employed the Hay-Wadt-pseudopotential-31(3d)G basis set for strontium [32, 39], the all-electron 86-411(31d)G basis set for titanium [32, 40]
and the 8-411(11d)G basis for oxygen [32, 41] with the exponentials for the d-GTOs set to 1.8 and 0.4. As fitting basis sets the MOLPRO Poisson (oxygen) [34], and GTO [35] converted into Poisson (titanium, strontium) [19] fitting sets of triple-zeta quality were used. The values for the distant-pair and very-distant pair cut-off thresholds were again set to 4 and 8 Å, respectively. The orbital domains covered the PAOs centered on the oxygen and two neighboring Ti atoms.

Table 1. Formal ionic and Mulliken charges for the SrTiO$_3$ crystal, calculated with HF, LMP2 and DFT methods.

| Atom | Formal ionic charges | Mulliken charges | HF | HF/LMP2 | LDA | PBE | B3LYP |
|------|----------------------|------------------|----|---------|-----|-----|------|
| Sr   | 2                    | 1.921            | 1.867 | 1.858 | 1.875 |
| Ti   | 4                    | 2.677            | 2.38 | 2.44   | 2.495 |
| O$^-$| 2                    | −1.533           | −1.416 | −1.433 | −1.456 |

The Mulliken charges were evaluated at the HF, HF/LMP2, DFT(LDA), DFT(PBE) and DFT(B3LYP) levels and are compiled in Table 1. In order to achieve convergence in the DFT calculations the level-shift technique [23] was employed. It can be seen from Table 1 that the LMP2 correction for the the Mulliken charges and thus for the density is small but still non-negligible and therefore can have an influence on various properties of this crystal. The correlated density tends to a lower ionicity, and this effect can become more pronounced with larger orbital basis sets and orbital domains employed, and also when the orbital relaxation is taken into account. The DFT method, which includes correlation to a certain extent, predicts a lower ionicity compared to the HF one as well, but apparently appears to overestimate this lowering, in particular if the LDA functional is used.

4. Conclusions
In this paper we have employed the Coupled Cluster Lagrangian approach, which is the standard scheme in molecular calculations of the first order properties at the correlated level, to calculate periodic LMP2 density matrices. Orbital relaxation effects have not yet been included. The calculations show that the LMP2 correction to the HF density matrix can be important for systems with a mixed covalent-ionic character of bonding. Orbital relaxation appears to be essential for the MP2 method, and, if taken into account, can noticeably improve the results. An implementation of orbital relaxed density matrices is deferred to future work.

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