Details and Features of the CRYSCOR Program.

http://www.cryscor.unito.it

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Part I

Local-MP2 for Periodic Systems
What is MP2?

**MP2** (Møller-Plesset Perturbation theory at second order) is the *simplest post-HF correlation technique*

Though inadequate in many respects (in particular, it is non-variational), it has several merits:

1) The MP2 energy $E^{(2)}$ is **size consistent**;
2) MP2 provides an adequate treatment of **long-range** interactions, dispersive interactions, hydrogen bonds and so on;
3) It allows the assessment of techniques, basis sets, etc., before introducing a more adequate treatment of short-range interactions (**MP4, CCSD**, …).
4) The MP2 correlation energy estimates can be corrected using the simple **Grimme SCS** (Spin-Component-Scaled) MP2 formula [[Grimme, J. Chem. Phys. 118 (2003) 9095](http://dx.doi.org/10.1063/1.1614909)], which proved to be very effective in a molecular context [[Hill, Platts, Werner, PCCP 8 (2006) 4072](http://dx.doi.org/10.1039/b514408a)].
What is **Local-MP2**?

Local representation of **occupied** and **virtual** HF manifold

**A truncation strategy can be adopted**

*Dynamical correlation effects are short-ranged.*

**Reformulation** of standard approaches (**MPn**, **CCSD(T)**, …)

![Bloch Functions](image)


**N--SCALING**

\[ N: \text{molecular size} \quad \rightarrow \quad n--\text{SCALING} \]

\[ n: \text{size of irred. part of crystal cell} \]
In this formulation the total MP2 energy is evaluated as a sum of local contributions, that is doubly excited configurations.

The excitation of a pair of electrons occurs from occupied local orbitals to virtual space.

\[
E_2 = \sum_{ij} \sum_{ab} K_{ab}^{ij} \left( 2T_{ab}^{ij} - T_{ba}^{ij} \right) = \sum_{ij} E_2^{ij}
\]

\[
K_{ab}^{ij} = (ia|jb) = \int \phi_i(r_1) \phi_a(r_1) \frac{1}{r_{12}} \phi_j(r_2) \phi_b(r_2) dr_1 dr_2
\]

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We start from the **local** non-canonical formulation of MP2 energy for closed shell systems:

\[
E_2 = \sum_{i} \sum_{j} \sum_{a} \sum_{b} K_{ab}^{ij} (2T_{ab}^{ij} - T_{ba}^{ij}) = \sum_{i} \sum_{j} E_{2}^{ij}
\]

\[
K_{ab}^{ij} = (ia|jb) = \int \phi_i(r_1)\phi_a(r_1) \frac{1}{r_{12}} \phi_j(r_2)\phi_b(r_2) \, dr_1 \, dr_2
\]

\[
R_{ab}^{ij} = K_{ab}^{ij} + \sum_{cd} \left\{ F_{ac}T_{cd}^{ij}S_{db} + S_{ac}T_{cd}^{ij}F_{db} - S_{ac} \left[ \sum_{k} (F_{ik}T_{cd}^{kj} + T_{cd}^{ik}F_{kj}) \right] S_{db} \right\} = 0
\]

In this formulation the total MP2 energy is evaluated as a sum of local contributions, that is doubly excited configurations. The excitation of a pair of electrons occurs from occupied local orbitals to virtual space.
Local Methods from Molecules to Crystals

\[ E_2 = \sum_{ij} \sum_{ab} K_{ab}^{ij} \left( 2T_{ab}^{ij} - T_{ba}^{ij} \right) = \sum_{ij} E_2^{ij} \]

\[ K_{ab}^{ij} = (ia|jb) = \int \phi_i(r_1) \phi_a(r_1) \frac{1}{r_{12}} \phi_j(r_2) \phi_b(r_2) dr_1 dr_2 \]

**Occupied Manifold**
Mutually Orthonormal and orthogonal to the virtual space

**Virtual Manifold**
Orthogonal to the occupied space but Redundant. Must be transformed to a Local OrthoNormal (LON) set.

The main ingredients of our method are Symmetry Adapted Wannier Functions (SAWFs), here and in the following indicated with latin letters (i,j) and Projected Atomic Orbitals (PAOs), indicated as (a,b).
Since all the quantities of interest (Fock matrix, overlap matrix, amplitudes, integrals) are translationally invariant, we redefine the correction energy as an energy per cell:

\[ E_2 = L E_{2}^{\text{cell}} \]

\[ E_{2}^{\text{cell}} = \sum_{i_0 j_g} E_2^{i_0 j_g} \]
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The first WF index is always in the zero cell.
MP2 in Crystals

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\[ E_2 = LE_2^{cell} \]

\[ E_2^{cell} = \sum_{i_0,j_0} E_{i_0,j_0}^{2} \]

The first WF index is always in the zero cell.

We are confined in a vicinity of the reference cell. The computation becomes \( \mathcal{O}(0) \) with respect to \( L \), and \( \mathcal{O}(n) \) with the size of the irreducible part of the reference cell. We are able to describe an infinite system.
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\[ E_2 = L E_{2}^{\text{cell}} \]

\[ E_{2}^{\text{cell}} = \sum \frac{E_2^{i_0 j_0}}{l_0 l_g} \]

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Part II

The CRYSCOR Program
Few Technical Remarks

The CRYSCOR program is entirely coded in FORTRAN90 programming language.

The only exception is the I/O library, which is coded in C for higher efficiency.

In the code algorithms who require large amounts of memory to are made such to fit in the available memory by using the disk if needed (paging). For this reason in the available memory must be specified in input.
**Standard Scheme of CRYSCOR**

1. Read Geometry, Symmetry, $S_{AO}, F_{AO}, SAWF$ from disk
2. Construct PAOs
3. Compute integrals
4. Self Consistent Solution of LMP2 Equations
5. MP2 Energy
6. MP2 correction to the Density Matrix

Mathematical expressions:

- $\chi_\alpha = \sum_\beta (1 - \hat{P})_{\alpha,\beta} \chi_\beta \rightarrow a$
- $K_{i\alpha}^{b\beta} = \sum_{\mu,\nu,\rho,\tau} c_{i\mu}^a c_{\nu}^a c_{\rho}^b c_{\tau}^b (\mu \nu | \rho \tau)$
- $R_{\alpha\beta}^{ij} \leq \epsilon$
- $\chi_{\alpha}^{LON} = \sum_{\alpha \in N_{LON}} X_{\alpha,\alpha}^{LON}$
- $E_{\text{cell}}^{(cell \ 0)} = \sum_i \sum_j \sum_{ab} K_{i\alpha}^{ab} (2T_{ij}^{ab} - T_{ij}^{ab})$
The most interesting feature of the local approach is that we are allowed to truncate summations according to thresholds. Here we present the most critical parameters for our calculation.

\[ \chi_{\alpha}^{LON} = \sum_{\alpha \in N_{LON}} X_{\alpha,\alpha} \chi_{\alpha} \]

\[ K_{ia}^{jb} = \sum_{\mu,\nu,\rho,\tau} c_{\mu} c_{\nu}^a c_{\rho}^j c_{\tau}^b (\mu \nu | \rho \tau) \]

\[ R_{ab}^{ij} \leq \epsilon \]

\[ E_{2}^{cell} = \sum_{i} \sum_{j} \sum_{ab} K_{ij}^{ab} (2T_{ij}^{ab} - T_{ij}^{ab}) \]
From our experience, “good” values for the computational parameters (errors ≈ 10^{-5} Ha) are:

- Maximum distance between core domains: d ≤ d_{max} ≈ 10 Å (extrapolation to infinite distance feasible with Lennard-Jones-Fitting Technique!)
- Excitation domain ≈ 2 stars of neighbors for ionic and covalent crystals, one molecule in the case of a molecular crystal
- Threshold on coefficients truncation = 10^{-4} or less
- Threshold for LON redundancy = 10^{-4}
The Role of Computational Parameters

When trying to optimize geometries (atomic positions, lattice parameter), or to simulate an adsorption of a molecule on a slab, it is important to keep fixed the effect of main computational thresholds, in order to obtain smooth potential curves.

This is conceptually similar to the FIXINDEX option in CRYSTAL

The main quantities to be frozen in our LMP2 are:

✓ Local Excitation Domains
✓ Number and type (integral approximation used) of pairs
✓ Number of redundant functions in the local domains.
Part III

The Integrals Evaluation
The bottleneck of the whole Local-MP2 method is represented by the calculation of 4 index integrals, which constitutes by itself about 99% of the whole time needed for a calculation.

The computational time amounts to several days even for the simplest system. This is due to the four index contraction over atomic orbitals needed to compute this integral between composite objects.

\[ K_{ab}^{ij} = \langle ia | jb \rangle = \int \phi_i(\mathbf{r}_1) \phi_a(\mathbf{r}_1) \frac{1}{r_{12}} \phi_j(\mathbf{r}_2) \phi_b(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \]

In order to be able to study systems of general interest it is mandatory to implement fast techniques to approximate these integrals.
The product distribution between Wannier function $i$ and PAO $a$ can be represented by a set of electric multipoles, $\{m_{(ia)}\}_{C}^{l}$, of maximum order $l$ and centered in $C$.

If the two distributions are sufficiently apart to be entirely contained in separate spheres, their electrostatic interaction can be approximated by a sum of interactions between the respective multipoles:

$$(ia|jb) = (\{m_{(ia)}\}_{C_1}^{l}|\{m_{(jb)}\}_{C_2}^{l})$$

Due to translational invariance only the multipoles in the zero cell need to be computed, all the others being the same.

Multipoles can be safely used for distances larger than 6 Å. Attention must be paid in the case of extended (augmented) basis sets and/or very large excitation domains.
Lennard-Jones Extrapolation

In molecular local correlation calculations very distant pairs can be safely neglected. In crystalline systems, these pairs can contribute significantly to the correlation energy.

This is due to the fact that the number of pairs included within a sphere grows quadratically with distance. This makes the multipolar approach itself inefficient for distances larger than, say, 12 Å.

On the other hand the distribution of atoms as a function of distance is known, and the energy contributions obey the $r^{-6}$ law. This allows us to extrapolate contribution up to large distances.

$$E_{2}^{LJ} \approx \frac{4\pi}{3} \frac{1}{r_{0}^{3}V_{cell}} \sum_{ij} c_{ij} n_{ij}$$

Where $ij$ labels the individual WF pair, $n_{ij}$ is the multiplicity, and the LJ coefficient $c_{ij}$ is determined by fitting of all the computed contributions below $r_{0}$. 
Lennard-Jones Extrapolation

LiH Bulk

![Graph showing Lennard-Jones extrapolation for LiH Bulk](graph.png)
Density Fitting is a powerful technique for integral evaluation that has widely proved its efficiency in molecular codes like MOLPRO. The basic idea is to expand product distributions in an Auxiliary Basis (e.g. gaussian functions $\{\Xi_i\}$). We will from now on refer to these functions with latin capital letters $P,Q$.

\[ \rho_{ia}(\mathbf{r}) = \phi_i(\mathbf{r}) \phi_a(\mathbf{r}) \approx \tilde{\rho}_{ia}(\mathbf{r}) = \sum_P d_{ia}^P \Xi_P(\mathbf{r}) \]

Fitting coefficients are determined by minimizing the error functional

\[ \Delta = \langle \rho_{ia} - \tilde{\rho}_{ia} | w_{12} | \rho_{jb} - \tilde{\rho}_{jb} \rangle \]

leading to the linear equation system

\[ \sum_P d_{ia}^P (P | Q) = (i a | Q) \]
So that the 4-index integrals are finally approximated as:

\[(ia|jb) \approx (ia|\tilde{jb}) = \sum_{P,Q} (ia|P)[J^{-1}]_{PQ}(Q|jb)\]

Only 3-center Coulomb integrals are needed.

The inverse matrix of 2-center coulomb integrals has the size of the number of auxiliary functions in the system.

where:

\[(ia|P) = \int \phi_i(r_1)\phi_a(r_1)r_{12}^{-1}\Xi_P(r_2)dr_1dr_2\]

and:

\[J_{PQ} = (P|Q) = \int \Xi_P(r_1)r_{12}^{-1}\Xi_Q(r_2)dr_1dr_2\]
Density Fitting in Periodic Systems

Three approaches

Reciprocal Space
Correction of the density
Instead of the true density, we fit a corrected density, suitably constructed so that it has no multipoles. This has still some stability issue.

Direct Space
Local Direct Fitting
(Almost) completely analogous to the one used in molecules

Reciprocal AND Direct Space
Direct Reciprocal Decoupled fitting
Two mutually orthogonal fitting sets are used, one in reciprocal space and another in direct space, and two fitting procedures are performed independently.

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08/09/09 MSSC2009
Density Fitting in Periodic Systems

We have seen that, thanks to translational symmetry, 4-index integrals are always referred to the zero cell

\[(i a | j b) \rightarrow (i_0 a_g | j_{\bar{g}} b_{\bar{g}'})\]

\(g, \bar{g}, \bar{g}'\) are lattice vector labels

This leads to the following expression for approximated integrals:

\[
(i_0 a_g | j_{\bar{g}} b_{\bar{g}'}) = \sum_{P, g_P, Q, g_Q} (i_0 a_g | P_{g_P}) [J^{-1}]_{P_{g_P}, Q_{g_Q}} (Q_{g_Q} | j_{\bar{g}} b_{\bar{g}'})
\]

3-index integrals are referred to the zero cell, all the others can be obtained by translation. In addition 3-center objects have, generally, higher point symmetry than 4-center ones.

Maschio, Usvyat, Manby et al. PRB 76, 075101 (2007)
Usvyat, Maschio, Manby et al. PRB 76, 075102 (2007)
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\]

Indices \(g_P, g_Q\) over lattice vectors should go very far, since they must, at least in principle, cover all the space spanned by all the possible i-j Wannier pairs, with their relative domains.

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\]

Inversion of a \(N \times N\) matrix scales as \(O(N^3)\). Inversion of such a big \(J\) matrix has high computational costs.
Density Fitting in Periodic Systems

The definition of Local fit-domains, different for each WF-PAO distribution, allows to solve these issues.

\[
\langle i_0 a_g | \tilde{j}_{\tilde{g}} b_{\tilde{g}'} \rangle = \sum_{P,g_P,Q,g_Q} \langle i_0 a_g | P_{g_P} \rangle [J^{-1}]_{P_{g_P},Q_{g_Q}} \langle Q_{g_Q} | j_{\tilde{g}} b_{\tilde{g}'} \rangle
\]

These summations are limited to a small number of centers. Usually 10 atoms are enough.
Performance of DFP

Timings for LMP2 calculations for diamond with 6–21G*
Dependence on the Wannier functions truncation threshold

CPU time, hours

LMP2

DF–LMP2

$-\log_{10}(TOL)$
Performance of DFP

<table>
<thead>
<tr>
<th>System</th>
<th>Basis set</th>
<th>Time LMP2</th>
<th>Time DF-LMP2</th>
<th>% Error on Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>6-21G*</td>
<td>16 days</td>
<td>4 min.</td>
<td>0.03%</td>
</tr>
<tr>
<td>Ice</td>
<td>6-311G**</td>
<td>4 days</td>
<td>15 min.</td>
<td>0.01%</td>
</tr>
<tr>
<td>CO₂</td>
<td>6-311G(3d)</td>
<td>2 days</td>
<td>30 min.</td>
<td>0.01%</td>
</tr>
<tr>
<td>MgO</td>
<td>8-511G*/8-411G*</td>
<td>19 h.</td>
<td>8 min.</td>
<td>0.01%</td>
</tr>
<tr>
<td>Ar</td>
<td>ECP/[4s4p3d2f]</td>
<td>10 days</td>
<td>5 min.</td>
<td>0.02%</td>
</tr>
</tbody>
</table>

Part IV

Conclusions
CRYSCOR Features

- MP2 Energy from the CRYSTAL HF solution
- MP2 Correction to the Density Matrix
- FULL exploitation of point and translational symmetry
- Fast evaluation of integrals
- Extrapolation of pair energies to infinite distance
- Fixing of indices (e.g. for lattice parameter optimizations)
- Possibility of Dual Basis Set technique to improve upon the HF basis set
How To Do It Right

✓ The CRYSTAL HF wavefunction must be of higher quality than usual - tighten ITOL4 and ITOL5. For instance:

```
TOLINTEG
7 7 7 15 50
```

✓ Choose carefully the local excitation domains:

If you compute binding energies, or cohesive energies, or relative stabilities, domains in different calculations must be compatible.

Try to understand how the localization has localized the orbitals, and if the domains are suitable according to “chemical” considerations (needs some experience!).

✓ Choose a basis set which is suitable for correlation - very good HF basis sets can be very poor for post-HF. Role of diffuse and polarization functions is very important!

✓ The fitting basis set should match the quality of the HF basis set

✓ Be aware of the approximations introduced by the use of local method and approximate integrals - energies can be trusted up to 0.1 mHartree

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Details and Features of the CRYSCOR Program
Future Prospects

Current work:
- Debugging - optimization - standardization - testing of the code
- Parallelization

In the next future...
- MP2 energy for geometry optimization (numerical gradients)
- CIS approach for excited states (Correction to the HF Band Gap)
- Improved estimates of electron density matrix correction
- Explicitly Correlated Methods (R12-F12)

...and more distant in time:
- Extension to other local correlation schemes (CC2, CCSD, MP4, ...)
- MP2 analytical gradients.
- Vibrational frequencies at the correlated level
- Dielectric Properties at the correlated Level
Thank you all for your kind attention