The coupled perturbed Hartree Fock (CPHF) treatment of the electric field perturbation for periodic systems; a new improvement of the CRYSTAL code.

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Understanding the behaviour of a system under the effect of an electric field (EF) has been a challenging task for many years.
The interaction between EF and matter generates a large variety of liner and non linear optical phenomena, starting from the induced dipole moment and the dielectric tensor of the crystalline system up to more complicated higher-order non linear effects.

The treatment of a periodic system under the effect of a static, constant electric field was already possible in the CRYSTAL03 code, by adding a sawtooth electric potential to the unperturbed HF or DFT Hamiltonian.
Calculations performed with the latter technique for the evaluation of the dielectric tensor for large unit cell systems (up to 80 atoms/cell) was incredibly expansive.

The new CPHF approach allows the determination of optical properties by performing the analytical derivation of the (HF) total energy with respect to the electric field (or generally to a small perturbation).
This approach provides in a faster, easier to use and much accurate way the dielectric tensor and higher order non linear optical properties.
The same approach can be use to study the effect of frequency-dependent electric field.

Further developments will permit, along the same lines, to access the extremely useful properties, such as piezoelectric tensor and Raman intensities.