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Coupled Perturbation Theory Approach to Dual Basis Sets for Molecules and Solids. I: General Theory and Application to Molecules.

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Abstract

We present a new coupled Hartree-Fock(HF)/Kohn-Sham DFT perturbation method that accounts for the effect of enlarging the basis set in electronic structure calculations. In contrast with previous approaches, our dual basis set treatment yields not only a correction for the total energy, but also for the orbital eigenvalues and density. The zero-th order solution is obtained from the projection of the small basis set coefficients. Diagonalization of the full Fock matrix in the large basis set is avoided. In this first paper of a series, we develop the theoretical foundations of our approach for molecules, including the coupled-perturbed equations through second order and the energy expressions through fourth order – as our method complies with Wigner’s $2n + 1$ rule. The first-order perturbation equation turns out to be uncoupled and odd-order terms in the energy expansion vanish.

In calculations on simple molecules, our method recovers over 93% (84%) of the missing DFT(HF) energy when going from the cc-pVDZ to the aug-cc-pVDZ basis,

and over about 95% in all cases if an energy extrapolation formula is used. Mulliken charges, orbital eigenvalue spectrum and HOMO-LUMO gaps of the large basis are well reproduced. Charge density maps show that the differences between the perturbatively corrected density and the reference nearly vanish through second-order.

1 Introduction

A major issue often encountered in electronic structure calculations involves dealing with large enough basis sets in order to achieve a desired high accuracy. For molecules the problem is mostly one of computation time; for solids there is the additional issue of achieving convergence in self-consistent field (SCF) treatments because of linear dependencies and numerical errors in truncation of the Ewald series.

In wavefunction methods a large virtual basis is needed to account for dynamic electron correlation whereas a smaller basis is sufficient to describe the occupied orbitals. This observation led Jurgens-Lutovsky and Almlöf¹ to propose a dual basis set scheme for MP2 calculations based on an approach introduced by King and co-workers^{2,3} for the description of Rydberg states. In their scheme¹ a small basis is augmented with additional basis functions so as to form a larger virtual space that is used to evaluate the MP2 perturbation sum. The additional virtual molecular orbitals needed for the MP2 calculation are determined by diagonalizing the Fock matrix obtained for the small basis Fock operator. Subsequently, Wolinsky and Pulay⁴ substantially improved the computational efficiency of this earlier treatment, based in large part on prescreening procedures taken from the local correlation approach.⁵ They also included a second-order perturbation theory correction for the single excitation terms that arise because Brillouin's theorem does not hold for the added virtuals in the large basis.

The situation is somewhat different with Kohn-Sham density functional theory. In that case correlation is included in the SCF equation that must be solved. Nonetheless, similar dual basis set procedures can be formulated. In particular, Liang and Head-Gordon⁶

presented the equivalent of a second-order perturbation scheme akin to the one described in Refs. 1,4 except that now the perturbation consists of just the single excitation terms. They also showed how the time-consuming diagonalization of the Kohn-Sham Fock matrix in the large virtual space could be replaced by iterative solution for the orbital coefficient matrix that couples the occupied and virtual spaces, followed by a simple trace relation for the energy lowering due to this coupling. The matrix equation is quadratic, but reduces to the perturbation scheme after making a linear approximation. This general approach has been extended by Steele, Head-Gordon and co-workers to include analytical derivatives for geometry optimization,⁷ MP2 theory,⁸ and other applications.⁹

Nakajima and Hirao¹⁰ have developed a dual-level approach to DFT that corrects for both basis set and lower level functional. Few years later Deng, Gilbert and Gill have developed a “triple jumping” approach,¹¹ that includes a correction for the integration grid as well.

More recently, Deng and Gill¹² have devised a different dual basis MP2 scheme, which utilizes the exact Hartree-Fock orbitals and energy in the large basis, but approximates the contribution of terms involving the extended basis functions to the MP2 energy. Their approach has the advantage that it does not require the small set to be a subset of the large one.

Finally, we mention the Perturbed AToms in MOlecules and Solids (PATMOS) treatment^{13,14} wherein the atom is the basic unit and the correlation energy is evaluated as a sum of intra- and inter-atomic terms; it is considered to be particularly well-suited for periodic systems. A large and a small basis is associated with each atom, but otherwise PATMOS falls into a distinctly different category from what are usually regarded as dual basis methods.

Our own interest in dual basis set methodology stems from its potential use in the calculation of solid state properties. In particular, we and our co-workers have devoted considerable effort to the development of coupled perturbed Hartree-Fock and Kohn Sham (CPHF/KS) methods for determining nonlinear optical properties,^{15,16} infrared¹⁷ and Raman^{18,19} vibrational intensities, piezoelectric coefficients, etc. of periodic systems. One problem with such

calculations is the choice of a basis set that is large enough to give accurate results without causing SCF convergence difficulties in solving the perturbation equations. In particular, diffuse (augmented) functions give rise to linear dependence and failed convergence of Ewald sums,^{20,21} often resulting in appearance of unphysical states in the solution. As a first step towards dealing with these issues we have formulated a general CPHF/CPKS treatment for the effect of a basis set extension on the HF/KS energy, which is the subject of the current paper that includes an application to molecules. This development opens the way to a systematic CPHF/CPKS dual basis set treatment of molecular properties that will ultimately allow us to take advantage of standard perturbation theory techniques, such as interchange relations^{22–25} and Wigner’s $2n+1$ rule,^{26,27} as we have done in the past.

In a similar fashion, we envisage our perturbative dual basis approach to be possibly combined with other perturbative treatments like MP2 for electron correlation.²⁸

In this first paper of a series we develop our new dual basis perturbation treatment in the context of molecular systems. As opposite to previous approaches, we derive coupled-perturbed equations through second order and energy expressions through fourth order, for both Hartree-Fock and DFT. This perturbation treatment allows us to correct the orbitals (hence density) and orbital energies, as well as to extrapolate to infinite order. In our next paper this treatment will be extended to periodic crystalline systems. An outline of the work presented here is as follows. In the next section we present a general definition of the dual basis set problem along with preliminary considerations. Then, in Section III we formulate the CPHF/CPKS dual basis set method, including our particular choice for the orders of perturbation theory and derivation of the perturbation energy expressions. In Section IV some results are presented in order to validate the method and benchmark its effectiveness. Finally, in the last section our important conclusions are drawn and future prospects are outlined.

2 From the small to the large basis set.

Let us start by defining two basis sets: a “small” one (S) and a “large” one (L). The SCF equation in the S basis is:

$${}^S\mathbf{F} {}^S\mathbf{C} = {}^S\mathbf{S} {}^S\mathbf{C} {}^S\epsilon \quad (1)$$

subject to the normalization condition

$${}^S\mathbf{C}^\dagger {}^S\mathbf{S} {}^S\mathbf{C} = {}^S\mathbf{1} \quad (2)$$

Here ${}^S\mathbf{F}$ is the electronic Fock matrix, which is the sum of a one-electron term, \mathbf{h} , and a two-electron term B :

$${}^S\mathbf{F} = {}^S\mathbf{h} + {}^S\mathbf{B} \quad (3)$$

The elements of \mathbf{B} are given by

$${}^SB_{\mu,\nu} = \sum_{\rho,\tau} {}^SD_{\tau\rho}(\mu\nu||\rho\tau) \quad (4)$$

where ${}^S\mathbf{D} = {}^S\mathbf{C} n {}^S\mathbf{C}^\dagger$ is the density matrix in the S basis.

2.1 Projection of the S solution onto the L basis

It is convenient to write the S basis functions, either approximately or exactly, in the L basis.

If the respective basis functions are denoted by a superscript S/L, then:

$$\sum_{\nu^L} a_{\nu^L}^{\nu^S} |\phi_{\nu^L}\rangle = |\phi_{\nu^S}\rangle \quad (5)$$

where $a_{\nu^L}^{\nu^S}$ are the combining coefficients. Multiplication of Eq. (5) on the left by $\langle\phi_{\mu^L}|$ gives:

$$\sum_{\nu^L} a_{\nu^L}^{\nu^S} \langle \phi_{\mu^L} | \phi_{\nu^L} \rangle = \langle \phi_{\mu^L} | \phi_{\nu^S} \rangle \quad (6)$$

Then, using the overlap matrix elements

$$\begin{aligned} {}^L S_{\mu^L, \nu^L} &= \langle \phi_{\mu^L} | \phi_{\nu^L} \rangle \\ {}^{LS} S_{\mu^L, \nu^S} &= \langle \phi_{\mu^L} | \phi_{\nu^S} \rangle \end{aligned} \quad (7)$$

we obtain

$$a_{\nu^L}^{\nu^S} = {}^{LS} P_{\nu^L, \nu^S} \quad (8)$$

with

$${}^{LS} \mathbf{P} = {}^L \mathbf{S}^{-1} {}^{LS} \mathbf{S} \quad (9)$$

Near linear dependencies can be detected and the corresponding small eigenvalues of ${}^L \mathbf{S}$ can be removed through an inversion by diagonalization procedure.

The basis set \mathbf{S} may or may not be entirely contained in \mathbf{L} . For simplicity, we will assume here that \mathbf{S} is a subset of \mathbf{L} . If not, there are several ways to extend the treatment, but we will leave that for future work.

Let us suppose we have solved the SCF equations in the \mathbf{S} basis to obtain ${}^S \mathbf{C}$. The zeroth order approximation for the *occupied* coefficients in the \mathbf{L} basis will then be:

$${}^L C_{\nu^L}^{j(0)} = \sum_{\nu^S} a_{\nu^L}^{\nu^S} {}^S C_{\nu^S}^j \quad (10)$$

or, in matrix notation:

$${}^L \mathbf{C}^{(0)} = {}^{LS} \mathbf{P} {}^S \mathbf{C} \quad (11)$$

Note that if the basis set \mathbf{S} was not exactly contained in \mathbf{L} , a reorthonormalization of the

occupied orbitals would be needed. It follows that, in zeroth order,

$${}^L\mathbf{D} = {}^L\mathbf{C} n {}^L\mathbf{C}^\dagger \quad (12)$$

then at zeroth order in the basis set perturbation, we have

$${}^L\mathbf{D}^{(0)} = {}^L\mathbf{C}^{(0)} n {}^L\mathbf{C}^{(0)\dagger} = {}^{LS}\mathbf{P} {}^S\mathbf{D} {}^{LS}\mathbf{P}^\dagger \quad (13)$$

Next we separate the space spanned by basis functions L into two subspaces, one of which is spanned by the S basis (\parallel) while the other (\perp) is orthogonal to it. For that purpose it is useful to define the matrix ${}^{SL}\mathbf{P}$:

$${}^{SL}\mathbf{P} = {}^S\mathbf{S}^{-1} {}^{SL}\mathbf{S} \quad (14)$$

Then, we introduce, the \mathbf{O}^\parallel matrix

$$\mathbf{O}^\parallel = {}^{LS}\mathbf{P} {}^{SL}\mathbf{P} \quad (15)$$

which represents the projection from the L space to the S space and back, together with its complementary matrix

$$\mathbf{O}^\perp = ({}^L\mathbf{1} - \mathbf{O}^\parallel) \quad (16)$$

A full derivation of these matrices and their main properties is reported in Appendix A. In particular, after projection onto S space it is shown in Appendix A that the matrix elements of any operator \hat{A} in the L basis are given by (see Eqs.(A.5)–(A.6)):

$$\mathbf{A}^{L,\parallel} = (\mathbf{O}^\parallel)^\dagger \mathbf{A}^L \mathbf{O}^\parallel \quad (17)$$

An exactly analogous relation holds for a prior projection onto the complementary space in L as well as the off-diagonal projections that couple the two spaces (see Eqs.(31) and (32)

below).

We also note that, for the *occupied* eigenvectors ${}^L\mathbf{C}_O^{(0)}$:

$$\mathbf{O}^\parallel {}^L\mathbf{C}_O^{(0)} = {}^{LS}\mathbf{P} {}^{SL}\mathbf{P} {}^{LS}\mathbf{P} {}^S\mathbf{C}_O = {}^{LS}\mathbf{P} {}^S\mathbf{C}_O = {}^L\mathbf{C}_O^{(0)} \quad (18)$$

and, thus,

$$\mathbf{O}^\perp {}^L\mathbf{C}_O^{(0)} = (\mathbf{1} - \mathbf{O}^\parallel) {}^L\mathbf{C}_O^{(0)} = {}^L\mathbf{C}_O^{(0)} - {}^L\mathbf{C}_O^{(0)} = \mathbf{0} \quad . \quad (19)$$

3 Basis set enlargement as a perturbation

Let us now assume that the differential effect of adopting L, as opposed to S, is sufficiently small so that the basis set enlargement can be considered as a perturbation. Then the coefficient matrix C can be expanded in orders of a perturbation parameter λ :

$$\mathbf{C} = \mathbf{C}^{(0)} + \lambda\mathbf{C}^{(1)} + \frac{1}{2!}\lambda^2\mathbf{C}^{(2)} + \frac{1}{3!}\lambda^3\mathbf{C}^{(3)} + \dots \quad (20)$$

where the zero-th order coefficients are those obtained directly after projection from the small basis— see Eq. (11). Here, as well as in the following, we have dropped the superscript L since all quantities from now on refer to the large basis. λ , as usual, is a formal parameter that varies between 0 and 1 and will ultimately be set equal to unity. As a consequence, the density matrix in orders of perturbation theory becomes:

$$\mathbf{D} = \mathbf{D}^{(0)} + \lambda\mathbf{D}^{(1)} + \frac{1}{2!}\lambda^2\mathbf{D}^{(2)} + \frac{1}{3!}\lambda^3\mathbf{D}^{(3)} + \dots \quad (21)$$

where:

$$\mathbf{D}^{(0)} = \mathbf{C}^{(0)} n \mathbf{C}^{(0)\dagger} \quad (22)$$

$$\mathbf{D}^{(1)} = \mathbf{C}^{(1)} n \mathbf{C}^{(0)\dagger} + \mathbf{C}^{(0)} n \mathbf{C}^{(1)\dagger} \quad (23)$$

$$\mathbf{D}^{(2)} = \mathbf{C}^{(2)} n \mathbf{C}^{(0)\dagger} + \mathbf{C}^{(0)} n \mathbf{C}^{(2)\dagger} + 2 \mathbf{C}^{(1)} n \mathbf{C}^{(1)\dagger} \quad (24)$$

For later use it is convenient to factor these matrices into block diagonal and block off-diagonal parts using the projection matrices \mathbf{O}^{\parallel} and \mathbf{O}^{\perp} .²⁹

$$\begin{aligned} \underline{\mathbf{D}}^{(n)} &= \mathbf{O}^{\parallel} \mathbf{D}^{(n)} \mathbf{O}^{\parallel\dagger} + \mathbf{O}^{\perp} \mathbf{D}^{(n)} \mathbf{O}^{\perp\dagger} \\ \overline{\mathbf{D}}^{(n)} &= \mathbf{O}^{\parallel} \mathbf{D}^{(n)} \mathbf{O}^{\perp\dagger} + \mathbf{O}^{\perp} \mathbf{D}^{(n)} \mathbf{O}^{\parallel\dagger} \end{aligned} \quad (25)$$

As in the case of \mathbf{C} and \mathbf{D} the Fock matrix $\mathbf{F} = \mathbf{h} + \mathbf{B}$ as well as the orbital energies, can be expanded as

$$\mathbf{F} = \mathbf{F}^{(0)} + \lambda \mathbf{F}^{(1)} + \frac{1}{2!} \lambda^2 \mathbf{F}^{(2)} + \frac{1}{3!} \lambda^3 \mathbf{F}^{(3)} + \dots \quad (26)$$

and

$$\epsilon = \epsilon^{(0)} + \lambda \epsilon^{(1)} + \frac{1}{2!} \lambda^2 \epsilon^{(2)} + \frac{1}{3!} \lambda^3 \epsilon^{(3)} + \dots \quad (27)$$

Since the bielectronic term depends linearly upon the density matrix it can be expressed as the sum of contributions from the block diagonal and block off-diagonal projections of \mathbf{D} , *i.e.*

$$\begin{aligned}
B_{\mu,\nu} [\mathbf{D}^{(n)}] &= B_{\mu,\nu} [\underline{\mathbf{D}}^{(n)}] + B_{\mu,\nu} [\overline{\mathbf{D}}^{(n)}] \\
&\equiv B_{\mu,\nu}[n] = B_{\mu,\nu}[\underline{n}] + B_{\mu,\nu}[\overline{n}]
\end{aligned} \tag{28}$$

where

$$B_{\mu,\nu} [\underline{\mathbf{D}}^{(n)}] = \sum_{\rho,\tau} \underline{\mathbf{D}}^{(n)} (\mu\nu \parallel \rho\tau) \equiv B_{\mu,\nu}[\underline{n}] \tag{29}$$

$$B_{\mu,\nu} [\overline{\mathbf{D}}^{(n)}] = \sum_{\rho,\tau} \overline{\mathbf{D}}^{(n)} (\mu\nu \parallel \rho\tau) \equiv B_{\mu,\nu}[\overline{n}] \tag{30}$$

Note that following Eq. (19) $\mathbf{B}[\bar{0}] = 0$, hence $\mathbf{B}[0] = \mathbf{B}[\underline{0}]$

3.1 Definition of perturbative orders of \mathbf{F}

In order to define orders of perturbation theory for the one- and two-electron matrices that contribute to \mathbf{F} we also partition these matrices into *diagonal* and *off-diagonal* blocks

$$\begin{aligned}
\underline{\mathbf{B}}[n] &= \mathbf{O}^{\parallel\dagger} \mathbf{B}[n] \mathbf{O}^{\parallel} + \mathbf{O}^{\perp\dagger} \mathbf{B}[n] \mathbf{O}^{\perp} \\
\overline{\mathbf{B}}[n] &= \mathbf{O}^{\parallel\dagger} \mathbf{B}[n] \mathbf{O}^{\perp} + \mathbf{O}^{\perp\dagger} \mathbf{B}[n] \mathbf{O}^{\parallel}
\end{aligned} \tag{31}$$

$$\begin{aligned}
\underline{\mathbf{h}} &= \mathbf{O}^{\parallel\dagger} \mathbf{h} \mathbf{O}^{\parallel} + \mathbf{O}^{\perp\dagger} \mathbf{h} \mathbf{O}^{\perp} \\
\overline{\mathbf{h}} &= \mathbf{O}^{\parallel\dagger} \mathbf{h} \mathbf{O}^{\perp} + \mathbf{O}^{\perp\dagger} \mathbf{h} \mathbf{O}^{\parallel}
\end{aligned} \tag{32}$$

Our separation of the various contributions to the Fock matrix \mathbf{F} in orders of perturbation

theory is as follows:

$$\mathbf{F}^{(0)} = \underline{\mathbf{h}} + \underline{\mathbf{B}}[\underline{0}] = \underline{\mathbf{h}} + \underline{\mathbf{B}}[0] \quad (33)$$

$$\mathbf{F}^{(1)} = \underline{\mathbf{B}}[\underline{1}] + \overline{\mathbf{h}} + \overline{\mathbf{B}}[0] = \boldsymbol{\Omega}^{(1)} \quad (34)$$

$$\mathbf{F}^{(2)} = \underline{\mathbf{B}}[\underline{2}] + 2\overline{\mathbf{B}}[\underline{1}] + 2\underline{\mathbf{B}}[\overline{1}] = \underline{\mathbf{B}}[\underline{2}] + 2\underline{\mathbf{B}}[\overline{1}] \quad (35)$$

$$\mathbf{F}^{(3)} = \underline{\mathbf{B}}[\underline{3}] + 3\overline{\mathbf{B}}[\underline{2}] + 3\underline{\mathbf{B}}[\overline{2}] + 6\overline{\mathbf{B}}[\overline{1}] \quad (36)$$

$$\begin{aligned} \mathbf{F}^{(n)} = & \underline{\mathbf{B}}[\underline{n}] + n\overline{\mathbf{B}}[\underline{n-1}] + n\underline{\mathbf{B}}[\overline{n-1}] \\ & + n(n-1)\overline{\mathbf{B}}[\overline{n-2}] \quad \text{for } n \geq 3 \end{aligned} \quad (37)$$

where we have introduced:

$$\boldsymbol{\Omega}^{(1)} = \overline{\mathbf{h}} + \overline{\mathbf{B}}[0] \quad (38)$$

and exploited the fact that $\underline{\mathbf{D}}^{(1)} = \mathbf{0}$. With this choice the off-diagonal AO blocks are systematically one order of perturbation theory higher than the diagonal blocks of the same matrix. As will be seen in the following, this definition guarantees Wigner's $2n+1$ rule,^{26,27} while the same proved not to be true for other choices we have considered. It is possible to use an alternative definition that will generate an $n+1$ rule. However, we prefer the formulation developed here because it leads to a number of simplifications including a convenient extrapolation procedure (*vide infra*).

3.2 Virtual spaces

Following our choice that the S basis should be entirely contained in L, the virtual MO manifold V in the L basis can be divided into two subspaces, that we will label as V' and V'' . V' contains the virtual orbitals of the S basis, while V'' contains the virtuals (orthogonal to V') that are added in the L basis. The additional V'' orbitals are obtained by diagonalizing the $\mathbf{O}^{\perp\dagger}\mathbf{F}^{(0)}\mathbf{O}^{\perp}$ matrix. We find this separation into V' and V'' subspaces advantageous because: i) it simplifies the formalism; and, ii) as we will show in more detail

for periodic systems in Paper II , it allows us to easily detect unphysical orbitals. Such unphysical orbitals, which can occur due to numerical inaccuracies in constructing the Fock matrix, are characterized by eigenvalues below the small basis HOMO (or Fermi level in periodic systems). For the V' space, Eqs. (18) and (19) hold, in exactly the same way as for the occupied orbitals (substitute V' for O). Conversely, for the V'' space we have, by construction,

$$\mathbf{O}^{\parallel} \mathbf{C}_{V''}^{(0)} = \mathbf{0} \quad ; \quad \mathbf{O}^{\perp} \mathbf{C}_{V''}^{(0)} = \mathbf{C}_{V''}^{(0)} \quad (39)$$

3.3 The orthonormality condition

By expanding the coefficient matrices in the orthonormality condition

$$\mathbf{C}^{\dagger} \mathbf{S} \mathbf{C} = \mathbf{1} \quad (40)$$

according to Eq. (20) and grouping orders of perturbation theory, we find:

$$\mathbf{C}^{(0)\dagger} \mathbf{S} \mathbf{C}^{(0)} = \mathbf{1} \quad (41)$$

$$\mathbf{C}^{(1)\dagger} \mathbf{S} \mathbf{C}^{(0)} + \mathbf{C}^{(0)\dagger} \mathbf{S} \mathbf{C}^{(1)} = \mathbf{0} \quad (42)$$

$$\mathbf{C}^{(2)\dagger} \mathbf{S} \mathbf{C}^{(0)} + 2\mathbf{C}^{(1)\dagger} \mathbf{S} \mathbf{C}^{(1)} + \mathbf{C}^{(0)\dagger} \mathbf{S} \mathbf{C}^{(2)} = \mathbf{0} \quad (43)$$

3.4 CPHF/CPKS perturbation equations

Except for the unique definition of orders the CPHF/CPKS perturbation equations are essentially the same as in our previous work.¹⁵ Thus, by inserting the expansions (26), (27) and (20) into the SCF equation $\mathbf{F} \mathbf{C} = \mathbf{S} \mathbf{C} \epsilon$ in the large basis, we obtain :

$$\mathbf{F}^{(0)}\mathbf{C}^{(0)} = \mathbf{S}\mathbf{C}^{(0)}\boldsymbol{\varepsilon}^{(0)} \quad (44)$$

$$\mathbf{F}^{(1)}\mathbf{C}^{(0)} + \mathbf{F}^{(0)}\mathbf{C}^{(1)} = \mathbf{S}\mathbf{C}^{(1)}\boldsymbol{\varepsilon}^{(0)} + \mathbf{S}\mathbf{C}^{(0)}\boldsymbol{\varepsilon}^{(1)} \quad (45)$$

$$\begin{aligned} \mathbf{F}^{(2)}\mathbf{C}^{(0)} + 2\mathbf{F}^{(1)}\mathbf{C}^{(1)} + \mathbf{F}^{(0)}\mathbf{C}^{(2)} &= \\ &= \mathbf{S}\mathbf{C}^{(2)}\boldsymbol{\varepsilon}^{(0)} + 2\mathbf{S}\mathbf{C}^{(1)}\boldsymbol{\varepsilon}^{(1)} + \mathbf{S}\mathbf{C}^{(0)}\boldsymbol{\varepsilon}^{(2)} \end{aligned} \quad (46)$$

...

The coefficient matrices may be expressed as

$$\mathbf{C}^{(n)} = \mathbf{C}^{(0)}\mathbf{U}^{(n)} \quad (47)$$

so that the orthonormalization conditions in Eqs. (41)–(43) become (through second-order)

$$\mathbf{U}^{(1)} = -\mathbf{U}^{(1)\dagger} \quad (48)$$

$$\mathbf{U}^{(2)} + \mathbf{U}^{(2)\dagger} = -2\mathbf{U}^{(1)\dagger}\mathbf{U}^{(1)} \quad (49)$$

Multiplication of Eqs.(45)–(46) on the left by $\mathbf{C}^{(0)\dagger}$ leads to a set of self-consistent equations for the $\mathbf{U}^{(n)}$ in terms of the matrices

$$\mathbf{G}^{(n)} = \mathbf{C}^{(0)\dagger}\mathbf{F}^{(n)}\mathbf{C}^{(0)} \quad (50)$$

The $\mathbf{G}^{(n)}$ matrices may be divided into blocks defined by the occupied O and virtual V' , V'' spaces. Explicit expressions for the various blocks, based on Eqs.(33)–(39), are given in Appendix B.

3.5 Non-canonical solution of first- and second-order perturbation equations

For sake of completeness, we develop here the coupled perturbed equations following the non-canonical treatment of Karna and Dupuis.²⁷ The first-order perturbation equation is:

$$\mathbf{G}^{(1)} + \boldsymbol{\varepsilon}^{(0)} \mathbf{U}^{(1)} = \mathbf{U}^{(1)} \boldsymbol{\varepsilon}^{(0)} + \boldsymbol{\varepsilon}^{(1)} \quad (51)$$

If i, j, \dots refer to occupied orbitals and a, b, \dots to virtuals, then assuming $\varepsilon_{ia}^{(1)} = 0$ the solution for the occ-virt elements of $\mathbf{U}^{(1)}$ is (switch i and a for the *virt-occ* elements)

$$U_{ia}^{(1)} = \frac{G_{ia}^{(1)}}{\varepsilon_a^{(0)} - \varepsilon_i^{(0)}} \quad (52)$$

with i occupied and a virtual. For the diagonal *occ-occ* and *virt-virt* blocks we make the particular non-canonical choice $U^{(1)} = U^{(1)\dagger} = 0$, which trivially satisfies Eq. (48).

Since $\underline{\mathbf{D}}^{(1)} = \mathbf{0}$ it is clear that only the $\mathbf{U}_{OV''}^{(1)}$ block is non-zero and a self-consistent solution of Eq. (51) is unnecessary because $\mathbf{G}_{OV''}^{(1)}$ does not contain the first-order density matrix (see Appendix B).

Given that the diagonal blocks of $\mathbf{U}^{(1)}$ vanish, it follows from Eq.(51) that:

$$\varepsilon_{ij}^{(1)} = G_{ij}^{(1)} \quad ; \quad \varepsilon_{ab}^{(1)} = G_{ab}^{(1)} \quad (53)$$

Finally, the *virt-virt* block of the Lagrange multiplier matrix through first-order can be diagonalized to give the virtual orbital energies through that order. In first-order the virtual orbital energies are modified due to V' , V'' coupling, but the occupied orbital energies are unaltered.

From Eq. (46) the second-order perturbation equation is:

$$\mathbf{G}^{(2)} + 2 \mathbf{G}^{(1)} \mathbf{U}^{(1)} + \boldsymbol{\varepsilon}^{(0)} \mathbf{U}^{(2)} = \mathbf{U}^{(2)} \boldsymbol{\varepsilon}^{(0)} + 2 \mathbf{U}^{(1)} \boldsymbol{\varepsilon}^{(1)} + \boldsymbol{\varepsilon}^{(2)} \quad (54)$$

Assuming that the *virt-occ* block of $\boldsymbol{\varepsilon}^{(2)}$ is zero, and using Eq. (49), we have:

$$U_{ai}^{(2)} = \frac{G_{ai}^{(2)} + 2 \sum_b^{virt} G_{ab}^{(1)} U_{bi}^{(1)} - 2 \sum_j^{occ} U_{aj}^{(1)} G_{ji}^{(1)}}{\varepsilon_i^{(0)} - \varepsilon_a^{(0)}} \quad (55)$$

Since the diagonal blocks of $\mathbf{U}^{(1)}$ and $\mathbf{U}^{(1)\dagger}$ are null it also follows from Eq. (49) that

$$U_{ia}^{(2)} = -U_{ai}^{(2)*} \quad . \quad (56)$$

By the same token the *occ-occ* block of $\mathbf{U}^{(2)}$ is obtained from Eq. (49) as $\mathbf{U}^{(2)} = -\mathbf{U}^{(1)\dagger} \mathbf{U}^{(1)}$, under the choice that this block is hermitian.

Based on the fact that $\overline{\mathbf{D}}^{(0)} = \mathbf{0}$ (and $\underline{\mathbf{D}}^{(1)} = \mathbf{0}$), we observe (see Appendix B) that $\mathbf{G}_{OV''}^{(2)} = \mathbf{0}$, which means that (see Eq.(55))

$$U_{V''O}^{(2)} = \mathbf{0} \quad (57)$$

that is, the second-order correction to the wavefunction does not couple the O and V'' spaces. A direct consequence of Eq. (57) is that $\overline{\mathbf{D}}^{(2)} = \mathbf{0}$.

The *occ-occ* block of the second-order Lagrange multiplier matrix can be obtained from Eq. (54) as

$$\begin{aligned} \varepsilon_{ij}^{(2)} &= G_{ij}^{(2)} + \sum_a^{virt} 2G_{ia}^{(1)} U_{aj}^{(1)} + U_{ij}^{(2)} (\varepsilon_i^{(0)} - \varepsilon_j^{(0)}) \\ &= G_{ij}^{(2)} + \sum_a^{virt} 2G_{ia}^{(1)} U_{aj}^{(1)} + \sum_a U_{ia}^{(1)} U_{aj}^{(1)} (\varepsilon_i^{(0)} - \varepsilon_j^{(0)}) \\ &= G_{ij}^{(2)} + \sum_a^{virt} U_{ia}^{(1)} U_{aj}^{(1)} (2\varepsilon_a^{(0)} - \varepsilon_i^{(0)} - \varepsilon_j^{(0)}) \end{aligned} \quad (58)$$

and, similarly, for the *virt-virt* block

$$\varepsilon_{ab}^{(2)} = G_{ab}^{(2)} + \sum_i^{occ} U_{ai}^{(1)} U_{ib}^{(1)} (2\varepsilon_i^{(0)} - \varepsilon_a^{(0)} - \varepsilon_b^{(0)}) \quad (59)$$

As before, the sum of the Lagrange multiplier matrices for the *occ-occ* block can be diagonalized to yield the occupied orbital energies – this time through second-order. The same holds for the *virt-virt* block.

3.6 Energy contributions

Starting from the Hartree-Fock energy expression (Tr signifies the trace)

$$E_{HF} = \frac{1}{2} Tr [(\mathbf{h} + \mathbf{F})\mathbf{D}] \quad (60)$$

and the perturbation expansion of the total energy

$$\mathbf{E} = \mathbf{E}^{(0)} + \lambda \mathbf{E}^{(1)} + \frac{1}{2!} \lambda^2 \mathbf{E}^{(2)} + \frac{1}{3!} \lambda^3 \mathbf{E}^{(3)} + \dots \quad (61)$$

we obtain the perturbation corrections to the energy through 4th-order given below. The full derivation is given in Appendix C

$$E_{HF}^{(0)} = \frac{1}{2} Tr [(\mathbf{h} + \mathbf{F}^{(0)}) \mathbf{D}^{(0)}] \quad (62)$$

$$E_{HF}^{(1)} = Tr [\mathbf{F}^{(0)} \mathbf{D}^{(1)}] = 0 \quad (63)$$

$$E_{HF}^{(2)} = Tr [\mathbf{\Omega}^{(1)} \mathbf{D}^{(1)}] \quad (64)$$

$$E_{HF}^{(3)} = Tr \left[6 \mathbf{U}_{OV}^{(1)\dagger} \left(\mathbf{U}_{VO}^{(1)} \mathbf{G}_{OO}^{(1)} - \mathbf{G}_{VV}^{(1)} \mathbf{U}_{VO}^{(1)} \right) + \frac{3}{2} \mathbf{\Omega}^{(1)} \mathbf{D}^{(2)} \right] = 0 \quad (65)$$

$$E_{HF}^{(4)} = Tr \left[12 \mathbf{U}_{OV}^{(1)\dagger} \left(2 \mathbf{G}_{VO}^{(1)} \mathbf{U}_{OO}^{(2)} + 2 \mathbf{G}_{VV}^{(1)} \mathbf{U}_{VO}^{(2)} - 2 \mathbf{U}_{VO}^{(2)} \mathbf{G}_{OO}^{(1)} + \mathbf{G}_{VV}^{(2)} \mathbf{U}_{VO}^{(1)} - \mathbf{U}_{VO}^{(1)} \mathbf{\epsilon}_{OO}^{(2)} \right) + \bar{\mathbf{B}}[\bar{\mathbf{I}}] \mathbf{D}^{(1)} \right] \quad (66)$$

Here $E_{HF}^{(0)}$ corresponds to the total energy as obtained in the small basis.

Note that:

$$Tr [\boldsymbol{\Omega}^{(1)} \mathbf{D}^{(1)}] = Tr [\boldsymbol{\Xi}^{(1)} \mathbf{U}^{(1)} n + \boldsymbol{\Xi}^{(1)} n \mathbf{U}^{(1)\dagger}] = 2 Tr [\boldsymbol{\Xi}_{OV''}^{(1)} \mathbf{U}_{V''O}^{(1)} + \boldsymbol{\Xi}_{V''O}^{(1)} \mathbf{U}_{OV''}^{(1)\dagger}] \quad (67)$$

where

$$\boldsymbol{\Xi}^{(1)} = \mathbf{C}^{(0)\dagger} \boldsymbol{\Omega}^{(1)} \mathbf{C}^{(0)} \quad (68)$$

$E_{HF}^{(3)}$ vanishes because $\overline{\mathbf{D}}^{(2)} = \mathbf{0}$ as do $\mathbf{G}_{OO}^{(1)}$, $\mathbf{G}_{V'V'}^{(1)}$ and $\mathbf{G}_{V''V''}^{(1)}$ (see Appendix B). Since $E_{HF}^{(4)}$ depends only on second-order quantities it is obvious that the $2n + 1$ is satisfied, at least through 4th-order – although we have no reasons to doubt its validity for higher orders.

3.6.1 Comparison with other approaches

It is of interest to compare our approach with the method of Martin Head-Gordon and coworkers (MHG in the following). Eq. (7) of Ref. 6 yields the dual basis set energy correction as

$$E^{MHG} = Tr [\mathbf{F}_{OV} \mathbf{X}_{VO}] \quad (69)$$

where \mathbf{F}_{OV} is the off-diagonal block of the Fock matrix constructed from $\mathbf{D}^{(0)}$ and thus equivalent to $\boldsymbol{\Xi}_{OV}^{(1)}$ in Eq. (68). The quantity

$$\mathbf{X}_{VO} = \mathbf{U}_{VO} \mathbf{U}_{OO}^{-1} \quad (70)$$

is introduced which in turn, is obtained as the solution of:

$$\mathbf{F}_{VO} + \mathbf{F}_{VV} \mathbf{X}_{VO} - \mathbf{X}_{VO} \mathbf{F}_{OO} - \mathbf{X}_{VO} \mathbf{F}_{OV} \mathbf{X}_{VO} = \mathbf{0}_{VO} \quad (71)$$

If limited to first order, so that $\mathbf{U}_{VO} = \mathbf{U}_{VO}^{(1)}$ and $\mathbf{U}_{OO} = \mathbf{1}_{OO}$, then Eq. (69) corresponds to our second-order energy in Eq. (64). As far as the initial Fock build is concerned, the two approaches are identical. Because of the last term on the lhs of Eq. (71) an infinite order

approximation for \mathbf{U} is actually obtained. Thus, the two treatments are equivalent through the second-order of perturbation theory, but diverge beyond that point.

Note that in the MHG approach, neither the correction to the wavefunction nor to the eigenvalues is provided.

From another point of view the “MP1” perturbation correction, which is the singles’ contribution to the MP2 energy due to violation of the Brillouin theorem, is usually expressed as:

$$E_{HF}^{MP1} = 2 \sum_{ia} \frac{\left(\mathbf{G}_{ia}^{(0)} + \mathbf{\Xi}_{ia}^{(1)}\right)^2}{\epsilon_i^{(0)} - \epsilon_a^{(0)}} = 2 \sum_{ia} \frac{\mathbf{\Xi}_{ia}^{(1)2}}{\epsilon_i^{(0)} - \epsilon_a^{(0)}} \quad (72)$$

since $\mathbf{G}_{OV}^{(0)} = \mathbf{0}$. Only those virtuals that belong to the V'' space will contribute to this sum. Making the appropriate substitutions from Appendix B and (52) into Eq.(72) leads to:

$$\begin{aligned} E_{HF}^{MP1} &= Tr \left[\mathbf{D}^{(1)}(\mathbf{h} + \mathbf{B}[0]) \right] \\ &= Tr \left[\mathbf{D}^{(1)}(\underline{\mathbf{h}} + \overline{\mathbf{h}} + \overline{\mathbf{B}}[0] + \underline{\mathbf{B}}[0]) \right] \\ &= Tr \left[\mathbf{D}^{(1)}(\overline{\mathbf{h}} + \overline{\mathbf{B}}[0]) \right] \end{aligned} \quad (73)$$

which, again, is our second-order energy – Eq. (64). Eq. (C.10) in Appendix C was used to obtain the last line in Eq. (72).

3.7 Energy Extrapolation

As one advantage of having obtained the separate energy corrections for different perturbation orders, an extrapolation to infinite order can be applied. Since the first- and third-order contributions are zero, we extrapolate using even orders only. For this extrapolation we employ the well-known formula

$$E_{HF}^{Extr} = E_{HF}^{(0)} - \frac{\left(E_{HF}^{(2)} - E_{HF}^{(0)}\right)^2}{E_{HF}^{(0)} - 2E_{HF}^{(2)} + E_{HF}^{(4)}} \quad (74)$$

Eq. (74) is usually attributed to Aitken,³⁰ but is actually much older as discussed in Ref. 31.

3.8 Density Functional Theory

Let us now consider the extension of our approach from CPHF to a Coupled-Perturbed Kohn-Sham (CPKS) treatment. We derive expressions for a hybrid functional, such as PBE0 or B3LYP, since local density and generalized gradient approximations are special cases, whereas the generalization to higher levels can be readily obtained.

In DFT calculations, the total electronic energy is separated into several terms³²

$$E_{DFT}^{(0)}(a_X) = E^T + E^V + E^J + a_X E_{HF}^X + E_R^{XC}(a_X) \quad (75)$$

In Eq. (75) E^T , E^V and E^J are the kinetic, electron-nuclear attraction and Coulomb repulsion energies, respectively. They are the same as in the HF treatment. E_{HF}^X is the HF exchange contribution $E_{HF}^X = Tr[\mathbf{B}^X \mathbf{D}]$, with \mathbf{B}^X being the exchange part of the bi-electronic term. It is multiplied by the scaling factor a_X to give the fraction of “exact” exchange in the functional. Finally, $E_R^{XC}(a_X)$ is the remaining exchange-correlation part of the electron-electron interaction energy.

The XC part of the DFT Fock matrix can be written as $F^{XC} = dE^{XC}/d\rho$ so that, following Pople et al.³²

$$\mathbf{F}_{DFT}^{XC} = \mathbf{F}_{DFT}^{XC}[\rho] = \sum_i w_i \left[\frac{\partial f^{XC}}{\partial \rho} \phi_\mu \phi_\nu + 2 \frac{\partial f^{XC}}{\partial |\nabla \rho|^2} \nabla \rho \cdot \nabla (\phi_\mu \phi_\nu) \right] \quad (76)$$

where f^{XC} is the exchange-correlation functional of the density, ρ , and its gradient, $\nabla \rho$, that yields E^{XC} when integrated over all space.

The additional Fock and energy contributions in our dual basis set perturbation treatment are similar to those obtained in other response treatments³³ (see, for instance, Eqs. (19) and

(20) of Ref. 34 for the case of electric fields in periodic systems). The key difference is the definition of orders in terms of the density matrix (or density) based on a separation of the latter into parallel and perpendicular projections. In exact analogy with our treatment of the Hartree-Fock exchange and (coulomb) terms \mathbf{F}_{DFT}^{XC} is expanded as (cf. Eqs. (33)–(37))

$$\begin{aligned}
\mathbf{F}_{DFT}^{XC(0)} &= \underline{\mathbf{F}}_{DFT}^{XC(0)}[\rho^{(0)}] \\
\mathbf{F}_{DFT}^{XC(1)} &= \overline{\mathbf{F}}_{DFT}^{XC(0)}[\rho^{(0)}] + \underline{\mathbf{F}}_{DFT}^{XC(1)}[\rho^{(1)}] \\
\mathbf{F}_{DFT}^{XC(2)} &= \overline{\mathbf{F}}_{DFT}^{XC(2)}[\rho^{(2)}] + 2\underline{\mathbf{F}}_{DFT}^{XC(2)}[\rho^{(1)}] \\
&\dots
\end{aligned} \tag{77}$$

It follows from Eq. (77) that the vanishing of odd-order terms proved for the Hartree-Fock treatment applies to DFT as well.

3.9 Implementation details

The present dual basis set method has been implemented in the Crystal code.³⁵ Despite being designed for the treatment of crystalline solids, this program is able to perform molecular calculations just like any standard molecular quantum chemistry program, thanks to the adoption of an atom-centered Gaussian basis set. Iterative solution of Eq. (54) is accelerated by means of DIIS techniques,^{36,37} which leads to convergence within 5-6 iterations, in all cases tested, at a threshold of 10^{-10} on the diagonal element of the DIIS error matrix.

The Xcfun library³⁸ is used for taking the functional derivatives. Plots have been realized using the CRYSPLOT online tool.³⁹

4 Results and Discussion

In this section we document the performance of our method for the total energy and compare with the treatment of Martin Head-Gordon and co-workers (hereafter referred to as the MHG method) – see Eqs. (69) - (71). We also analyze the effect of the basis set corrections on the eigenvalue spectrum, (Mulliken) atomic charges and electronic densities, which cannot be computed using other approaches.

Since our ultimate goal is to be able to use diffuse functions for systems – like crystalline solids – in which their use is not possible otherwise, we have mostly adopted the pairing of cc-pVXZ with the corresponding aug-cc-pVXZ basis, but any other pairing such that the S basis is entirely contained in L would be feasible with our current formalism. Since the main purpose of this work is to validate the method, we leave for future studies an extensive benchmark of basis set pairings. In most instances our results were obtained with Hartree-Fock and the popular representative hybrid functional PBE0. Molecular geometries are available as supplementary material. Finally, for convenience, we refer to our method as MKn , where n stands for the perturbation order, and employ the notation $MKn_{S-basis}^{L-basis}$ to include the definition of the two basis sets.

We will not present detailed timings here, as our main concern is to validate the method and focus on accuracy. However, it might be of interest to the reader to present at least some analysis. The Fock matrix build in the large basis is the rate-determining step in our largest test calculation – C₆H₆ molecule with cc-pVTZ/aug-cc-pVTZ basis set. In the large-basis SCF convergence is achieved in 10 iterations. Just one Fock build is performed in the MHG method, while our uncoupled MKn approach requires one build per each perturbative order (including zero-th order). In the case of coupled-perturbed iterations, 3 additional builds at second-order are needed, which is still 30% less than for the full large-basis SCF.

4.1 Energies

Table 1 reports the MKn total energy corrections for a set of small molecules, when cc-pVDZ is used as the S basis and the L basis is aug-cc-pVDZ. It is seen that the 2nd order correction recovers about 62-73% of the missing total energy at the HF level, 75-86% in the DFT case.

The fourth-order correction is decisive in achieving high accuracy - in all cases about 84-92% of the missing total energy for HF, 93-97% for DFT. Extrapolation using Eq. (74) leads to values that are remarkably close to the reference, with absolute differences well below 0.5 milliHartree and a recovery of more than about 95% in all cases. These observations remain qualitatively the same for the uncoupled treatment wherein Eq. (55) is solved non-iteratively, except that the extrapolations do not work nearly as well. In particular, for the DFT calculations they typically lead to a significant overcorrection.

Comparing the MKn results with the MHG ones, we note that the latter are slightly better than our second-order energies, but not quite as good as our $E^{(4)}$ values, with the latter difference being more substantial after extrapolation. Except for the effect of extrapolation, these observations again remain much the same for the uncoupled treatment. Even so, the magnitude of the error is less than for the MHG method (except in one case). For DFT there is a tendency in the MHG method to overcorrect⁴⁰ (an empirical scaling factor has been proposed to compensate for that effect). We note that the coupled perturbed iterations in our second-order equation substantially relieve this tendency (compare the coupled and uncoupled calculations in fourth-order).

A somewhat similar analysis pertains to augmentation of the correlation consistent triple-zeta basis set – see Table 2. Now the zeroth-order energy differences are smaller, which leads to reduced values for the percentage recovery. The absolute errors at second- and fourth-order are less than in Table I, being smaller than 1 milliHartree in all cases, while the energy extrapolation seems to be slightly less effective than in the double-zeta case. Thus, the extrapolated energies do not represent an improvement over the MHG method in a couple of the DFT calculations.

On the other hand, omitting the SCF iterations in second-order does not now lead to overcorrections in the DFT case. Both at fourth-order and after extrapolation, the uncoupled treatment yields values that are quite similar to the coupled calculations. This behavior deserves further study since, if general, it would lead to a much more efficient procedure. It may be that iterative treatment of the MK2 equations is necessary only if the reference basis is of double zeta quality or less.

It is instructive, in view of the future development of gradients within our dual basis method, to briefly investigate potential energy surfaces. A common test case is the HF binding energy curve for a neon dimer, which is shown in Figure 1. In the infinite basis set limit the bond between the two atoms is non-existent, since HF cannot describe dispersion interactions.⁴¹ However, in a finite basis the basis superposition error will give rise to a minimum that, for a small cc-pVDZ basis, occurs at a shorter internuclear distance than a larger d-aug-cc-pVDZ basis. As seen in the figure the coupled perturbed basis set corrections progressively shift the cc-pVDZ curve so that, in fourth-order, it is almost parallel to the doubly-augmented reference; extrapolation brings the two curves slightly closer to one another and more nearly parallel.

Table 1: Absolute errors in the coupled perturbed energy (in milliHartree) for a set of simple molecules computed at the Hartree-Fock (top) and PBE0 (bottom) levels. Values for the corresponding uncoupled (non-iterative) treatment are given in parentheses. S basis: cc-pVDZ; L basis: aug-cc-pVDZ E^{Ref} is the reference value for the aug-cc-pVDZ basis (in Hartree). ΔE^{MHG} refers to Martin Head-Gordon’s approach.⁶

Molecule	$\Delta E^{(0)}$	$\Delta E^{(2)}$	$\Delta E^{(4)}$	ΔE^{Extr}	ΔE^{MHG}	E^{Ref}	
Hartree – Fock	LiH	0.54	0.18	0.07 (0.08)	0.02 (0.04)	0.13	-7.984187
	NH ₃	9.93	3.82	1.47 (1.63)	0.02 (0.40)	2.89	-56.205423
	H ₂ O	14.44	5.00	1.72 (1.75)	-0.03 (0.05)	3.68	-76.040752
	HCN	4.26	1.22	0.39 (0.41)	0.08 (0.12)	0.91	-92.886575
	CO ₂	11.68	3.20	0.95 (0.99)	0.13 (0.21)	2.07	-187.663237
	HCOOH	15.85	4.65	1.46 (1.54)	0.18 (0.34)	3.24	-188.794243
	CH ₄ N ₂ O	22.68	6.92	2.28 (2.42)	0.34 (0.62)	4.92	-224.024602
	C ₆ H ₆	6.06	1.62	0.51 (0.58)	0.14 (0.26)	1.23	-230.728219
PBE0	LiH	0.59	0.10	0.04 (0.04)	0.03 (0.03)	0.04	-8.048678
	NH ₃	14.47	3.68	0.95 (0.50)	0.02 (-0.82)	1.23	-56.205423
	H ₂ O	20.85	4.72	1.01 (-0.19)	-0.10 (-2.34)	1.17	-56.499660
	HCN	5.53	1.08	0.28 (0.16)	0.10 (-0.08)	0.38	-93.320557
	CO ₂	13.57	2.71	0.64 (0.33)	0.16 (-0.34)	0.72	-188.413993
	HCOOH	19.39	4.07	0.98 (0.48)	0.20 (-0.61)	1.20	-189.588405
	CH ₄ N ₂ O	28.69	6.24	1.56 (0.80)	0.32 (-0.94)	1.86	-225.058198
	C ₆ H ₆	8.65	1.23	0.26 (0.22)	0.12 (0.07)	0.51	-231.990437

Table 2: Absolute errors in the coupled perturbed energy (in milliHartree) for a set of simple molecules computed at the Hartree-Fock (top) and PBE0 (bottom) levels. Values for the corresponding uncoupled (non-iterative) treatment are given in parentheses. S basis: cc-pVTZ; L basis: aug-cc-pVTZ E^{Ref} is the reference value for the aug-cc-pVTZ basis (in Hartree). ΔE^{MHG} refers to Martin Head-Gordon’s approach.⁶

Molecule		$\Delta E^{(0)}$	$\Delta E^{(2)}$	$\Delta E^{(4)}$	ΔE^{Extr}	ΔE^{MHG}	E^{Ref}
Hartree – Fock	LiH	0.18	0.06	0.02 (0.03)	0.01 (0.01)	0.03	-7.986830
	NH ₃	2.51	1.16	0.60 (0.64)	0.23 (0.33)	0.71	-56.220379
	H ₂ O	3.43	1.44	0.63 (0.68)	0.09 (0.22)	0.89	-76.059844
	HCN	1.05	0.38	0.17 (0.18)	0.07 (0.09)	0.17	-92.908105
	CO ₂	2.25	0.79	0.32 (0.34)	0.09 (0.14)	0.35	-187.710057
	HCOOH	3.35	1.19	0.47 (0.51)	0.11 (0.20)	0.65	-188.840965
	CH ₄ N ₂ O	5.13	1.94	0.81 (0.88)	0.19 (0.35)	1.11	-224.077896
	C ₆ H ₆	1.86	0.63	0.25 (0.28)	0.09 (0.13)	0.35	-230.781228
PBE0	LiH	0.34	0.07	0.02 (0.02)	0.01 (0.01)	0.02	-8.051777
	NH ₃	3.68	1.47	0.76 (0.76)	0.43 (0.42)	0.36	-56.515711
	H ₂ O	5.57	1.96	0.78 (0.74)	0.19 (0.10)	0.44	-76.379839
	HCN	1.20	0.35	0.15 (0.15)	0.09 (0.09)	0.07	-93.342724
	CO ₂	2.53	0.77	0.30 (0.29)	0.12 (0.12)	0.15	-188.459636
	HCOOH	4.18	1.30	0.48 (0.28)	0.17 (0.17)	0.29	-189.633984
	CH ₄ N ₂ O	6.69	2.21	0.88 (0.87)	0.31 (0.30)	0.51	-225.110792
	C ₆ H ₆	1.87	0.37	0.11 (0.12)	0.06 (0.06)	0.10	-232.042280

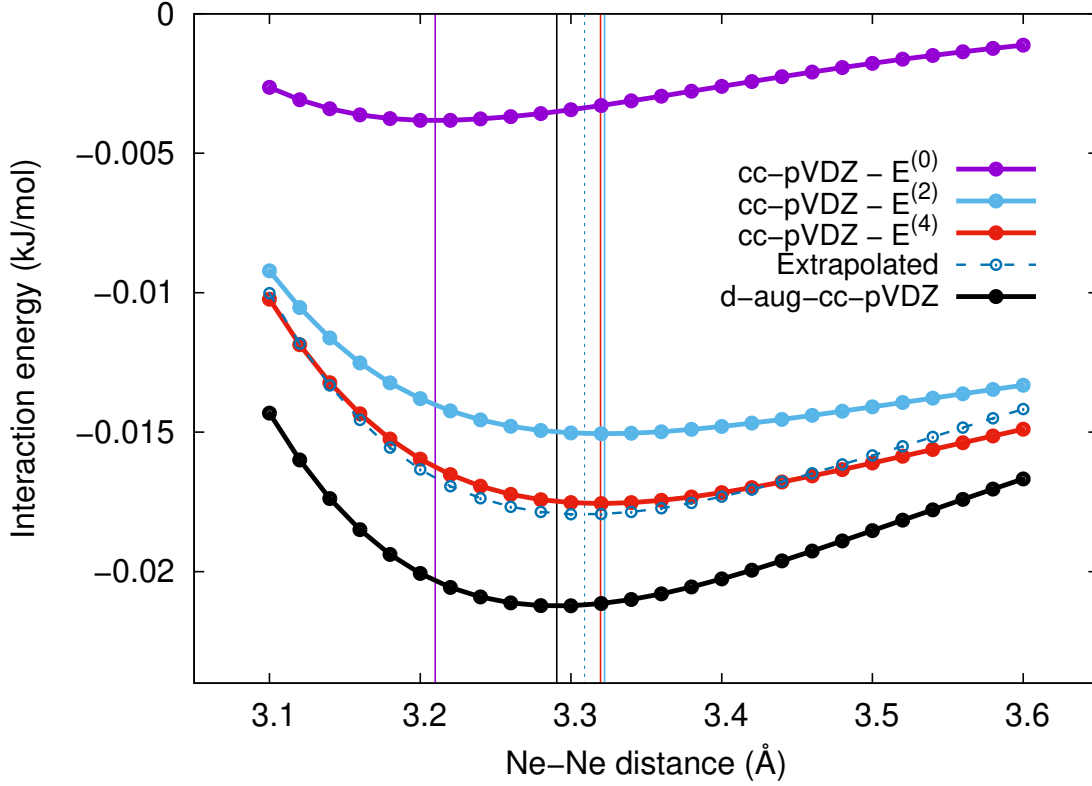


Figure 1: Interaction energy in Ne dimer as a function of distance between the two atoms using cc-pVDZ as a small basis and d-aug-cc-pVDZ as a large basis, computed at the Hartree-Fock level. Vertical lines indicate positions of minima, as obtained from a Morse potential fit.

4.2 Properties

4.2.1 Orbital Energy Levels

In Figure 2 we display the eigenvalue spectrum of the water molecule, as obtained with the $S = \text{cc-pVDZ}$ (left) and $L = \text{aug-cc-pVDZ}$ (right) basis sets at the PBE0 level (cf. Eqs. (53), (58) and (59)). In between are the diagonalization of the full $\mathbf{F}^{(0)}$ matrix (as performed in the MHG method), and our first- and second-order CPHF corrected MK1 and MK2 results. At the uncorrected cc-pVDZ level, we also show the eigenspectrum obtained from diagonalization of the *perp-perp* block of the 0-th order Fock matrix (V'' space - see Section 3.2).

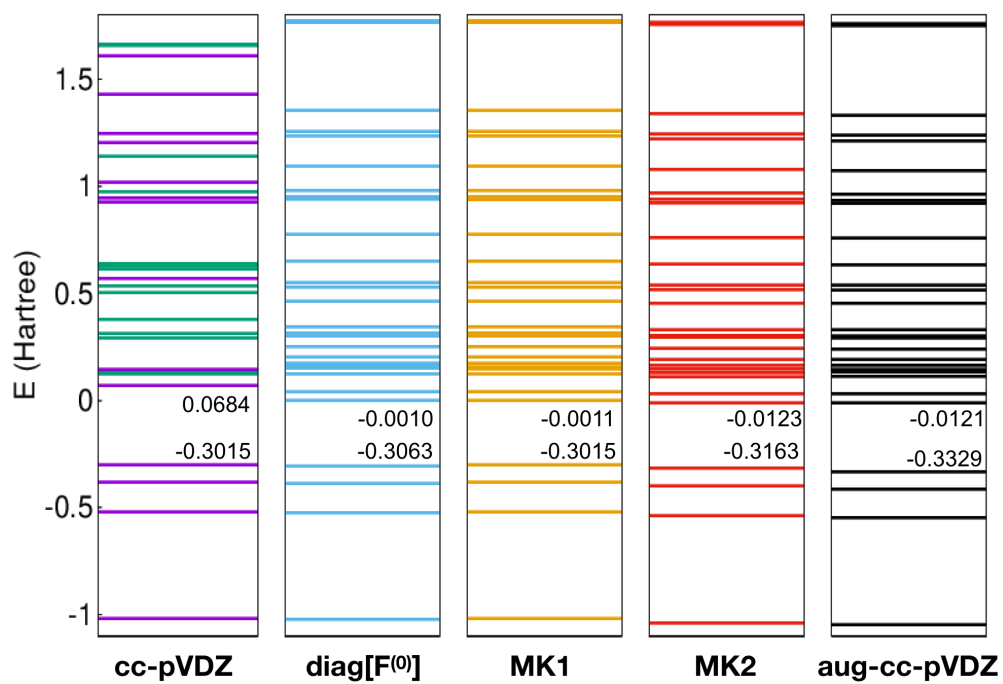


Figure 2: Graphical representation of the eigenvalue spectrum around the HOMO-LUMO gap for the water molecule (PBE0). In the left panel we report in green color the eigenvalues obtained from the diagonalization of the *perp-perp* block of the Fock matrix in the L basis (V'' space). Values for the HOMO and LUMO levels are reported explicitly.

We observe that the HOMO-LUMO gap is much too large for the cc-pVDZ basis. None of the additional orbitals just described falls in this gap, although this can happen. The first order correction (MK1) significantly corrects the virtual orbitals, leading to a gap that is closer to the reference. On the other hand, at this level no change occurs in the occupied orbitals, as expected. The second-order (MK2) correction acts on the occupied levels bringing them close to the reference values. The virtuals are also slightly corrected at this order. The diagonalization of the full $\mathbf{F}^{(0)}$ matrix – that is avoided in our MK n method – leads to virtual energy levels almost identical to our MK1 result, and occupied levels that fall in between MK1 and MK2.

A more extensive analysis of the effect of basis set corrections on HOMO-LUMO gaps is reported in Table 3. Here it is observed that the behavior just discussed in the case of the water molecule seems to be general, as the reference gap is accurately and, in most instances, steadily approached when going from MK0 to MK1 and MK2. In all cases, the main correction is seen at the MK1 level.

4.2.2 Electronic Charge

Thanks to the availability of corrections to the density matrix our method enables us compute a wide variety of properties. In that regard, it is of interest to examine the electronic charge density itself. Figure 3 shows difference maps for the charge density between the reference L basis (aug-cc-pVDZ) and the $\text{MK}n_{cc-pVDZ}^{aug-cc-pVDZ}$ corrected densities for the planar urea molecule. In zeroth-order significant differences are observed, especially near the atomic positions. There is an evident deficiency of electronic charge around the H atoms. This is reflected in the Mulliken charges (see Table 4), which also indicate an excess of electronic charge on the C atom. Although Mulliken charges are known not to provide a reliable partitioning of electronic charge when a diffuse basis set is employed, we are using them here simply to quantify how well our perturbation treatment reproduces the electronic charge transfer due to basis set extension. The MK1 correction significantly reduces these

discrepancies in Fig. 3 leaving a clear difference only near oxygen; it also leads to Mulliken charges that are very similar to the reference. Finally, MK2 yields a density that has only small differences with respect to aug-cc-pVDZ. The uncoupled treatment behaves similarly, although a larger error is observed in the core region of the O and N atoms after corrections are included. An analogous behavior is seen in Figure 3 and in Table 4 for benzene and HCN. In either case the first-order correction already yields an excellent agreement with the reference for Mulliken charges, although a significant overcorrection of the density around the N atom is observed in HCN.

Table 3: Hartree-Fock and PBE0 HOMO-LUMO gaps in eV.

molecule		cc-pVDZ	MK1 ^{aug-cc-pVDZ} _{cc-pVDZ}	MK2 ^{aug-cc-pVDZ} _{cc-pVDZ}	aug-cc-pVDZ
Hartree – Fock	LiH	8.20	7.96	7.96	7.97
	NH ₃	16.44	12.34	12.34	12.58
	H ₂ O	18.43	14.42	14.52	14.82
	HCN	18.08	14.18	14.23	14.29
	CO ₂	20.57	16.12	16.19	16.32
	HCOOH	17.27	13.49	13.58	13.74
	CH ₄ N ₂ O	14.86	11.24	11.33	11.59
	C ₆ H ₆	12.82	10.07	10.08	10.13
PBE0	LiH	4.35	4.32	4.36	4.30
	NH ₃	9.13	7.08	7.08	7.50
	H ₂ O	10.07	8.17	8.27	8.73
	HCN	10.75	10.22	10.25	10.27
	CO ₂	11.76	10.46	10.56	10.64
	HCOOH	8.30	7.98	7.99	8.10
	CH ₄ N ₂ O	7.87	6.26	6.35	6.67
	C ₆ H ₆	7.17	7.00	6.98	7.01

Table 4: Mulliken charges for urea, benzene and HCN molecules, as obtained at different perturbation orders for the PBE0 functional.

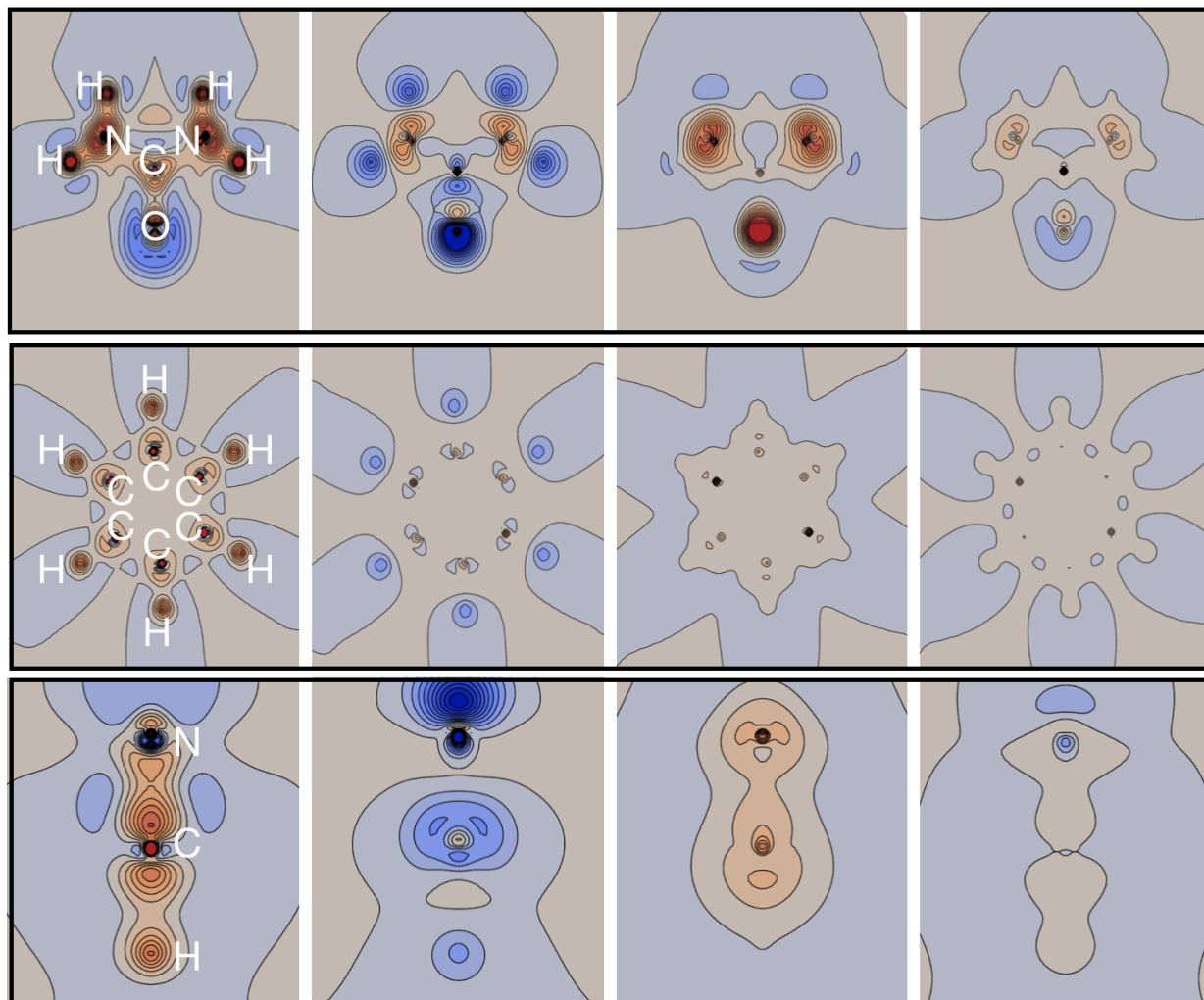
	Atom	cc-pVDZ	MK1 $_{cc-pVDZ}^{aug-cc-pVDZ}$	MK2 $_{cc-pVDZ}^{aug-cc-pVDZ}$	aug-cc-pVDZ
Urea	C	5.81	5.11	5.09	4.97
	O	8.36	8.59	8.59	8.64
	N	7.13	7.02	7.05	7.06
	H	0.87	1.05	1.04	1.05
	H	0.91	1.07	1.07	1.08
C ₆ H ₆	C	6.00	5.46	5.46	5.41
	H	1.00	1.54	1.54	1.59
HCN	H	0.89	1.01	1.01	1.00
	C	5.99	5.66	5.67	5.61
	N	7.11	7.33	7.32	7.39

5 Conclusions

We have developed a novel coupled perturbation theory treatment of dual basis sets that introduces the basis set enlargement as a perturbation with respect to the small basis solution. In contrast with previous approaches our method yields corrected Hartree-Fock/Kohn-Sham DFT orbitals and orbital energies, thereby allowing for the subsequent calculation of properties along with total energies. As it turns out, odd orders in the energy expansion are zero and the first-order perturbation equation is uncoupled. Our approach satisfies Wigner’s $2n+1$ rule. Hence, the second-order coupled perturbed solutions determine energy corrections through fourth order. A straightforward extrapolation appears to work effectively.

Illustrative energy calculations are carried out on a number of small molecules (plus the neon dimer) and the corrected small basis set values are seen to be quite close to those found for the large basis set. They also compare well with results obtained using the earlier dual basis set method of Martin Head-Gordon and co-workers. Representative calculations of orbital energies and electron densities are also presented. Again, our coupled perturbation theory closely reproduce those computed directly with the large basis set.

We are already working on the extension to periodic systems, that are our main interest, in the belief that the methodology developed here will foster the use of gaussian basis sets for



A) Δ -cc-pVDZ

B) Δ -MK1

C') Δ -MK2 (unc.)

C) Δ -MK2

Figure 3: Effect of MKn basis set corrections on the total charge density of urea (top), benzene (center) and HCN (bottom) molecules using the PBE0 functional. A) Difference map between total electronic charge computed with the aug-cc-pVDZ and cc-pVDZ basis sets. B) and C) : same as A) but with respect to the $MK1_{cc-pVDZ}^{aug-cc-pVDZ}$ and $MK2_{cc-pVDZ}^{aug-cc-pVDZ}$ levels of correction, respectively. C') is the same as C) , but in the uncoupled treatment. The isolines are spaced by 0.001 Bohr. Colors from blue to red range from the largest negative to the largest positive difference.

such systems. While in the current work our focus was on the development and validation of the theory, we also plan to carry out extensive benchmarks. This will be useful in addressing the practicalities for everyday use of the algorithm, such as the choice of optimal basis set pairings.

Supporting Information

In the SI we report the geometries of the molecules of our small test set.

Appendix

A Parallel and Orthogonal subspaces

Let us start from the definition of the identity operators in the two bases:

- The identity operator in L space is

$$\hat{I}^L = \sum_{\mu^L, \nu^L} |\mu^L\rangle S_{\mu^L, \nu^L}^{-1} \langle \nu^L| \quad (\text{A.1})$$

- The identity operator in S space is

$$\hat{I}^S = \sum_{\mu^S, \nu^S} |\mu^S\rangle S_{\mu^S, \nu^S}^{-1} \langle \nu^S| \quad (\text{A.2})$$

- The projection of an operator A onto the large basis is given by:

$$\hat{A}^L = \hat{I}^L \hat{A} \hat{I}^L \quad (\text{A.3})$$

with matrix elements:

$$A_{\mu^L, \nu^L} = \langle \mu^L | \hat{I}^L \hat{A} \hat{I}^L | \nu^L \rangle = \langle \mu^L | \hat{A} | \nu^L \rangle \quad (\text{A.4})$$

The projection of the operator \hat{A}^L onto the smaller basis and back to L may, then, be expressed as

$$\hat{A}^{L,\parallel} = \hat{I}^L \hat{I}^S \hat{A}^L \hat{I}^S \hat{I}^L = (\hat{O}^{\parallel})^\dagger \hat{A}^L \hat{O}^{\parallel} \quad (\text{A.5})$$

$$\begin{aligned}
\langle \mu^L | \hat{A}^S | \nu^L \rangle &= \langle \mu^L | \hat{I}^S \hat{I}^L \hat{A} \hat{I}^L \hat{I}^S | \nu^L \rangle \\
&= \mathbf{O}^{\parallel \dagger}_{\mu^L, \tau^L} \mathbf{A}_{\tau^L, \sigma^L} \mathbf{O}^{\parallel}_{\sigma^L, \nu^L}
\end{aligned} \tag{A.6}$$

where the projection matrix

$$\mathbf{O}^{\parallel}_{\sigma^L, \mu^L} = {}^{LS}P_{\sigma^L, \tau^S} {}^{SL}P_{\tau^S, \mu^L} \tag{A.7}$$

with

$${}^{LS}P_{\sigma^L, \tau^S} = \sum_{\rho^L} [{}^L S^{-1}]_{\sigma^L, \rho^L} \langle \rho^L | \tau^S \rangle \tag{A.8}$$

and

$${}^{SL}P_{\sigma^S, \tau^L} = \sum_{\rho^S} [{}^S S^{-1}]_{\sigma^S, \rho^S} \langle \rho^S | \tau^L \rangle \tag{A.9}$$

The complementary projection matrix is simply :

$$\mathbf{O}^{\perp} = ({}^L \mathbf{1} - {}^{LS} \mathbf{P} {}^{SL} \mathbf{P}) = ({}^L \mathbf{1} - \mathbf{O}^{\parallel}) \tag{A.10}$$

and it is easily verified that:

$$\mathbf{O}^{\perp} \mathbf{O}^{\parallel} = \mathbf{O}^{\parallel} \mathbf{O}^{\perp} = \mathbf{0} \tag{A.11}$$

Since

$${}^{SL} \mathbf{P} {}^{LS} \mathbf{P} = {}^S \mathbf{1} \tag{A.12}$$

it is straightforward to verify idempotency relations

$$\mathbf{O}^{\parallel} \mathbf{O}^{\parallel} = {}^{LS} \mathbf{P} {}^{SL} \mathbf{P} {}^{LS} \mathbf{P} {}^{SL} \mathbf{P} = {}^{LS} \mathbf{P} {}^{SL} \mathbf{P} = \mathbf{O}^{\parallel} \tag{A.13}$$

$$\mathbf{O}^{\perp} \mathbf{O}^{\perp} = \mathbf{1} - 2\mathbf{O}^{\parallel} + \mathbf{O}^{\parallel} \mathbf{O}^{\parallel} = \mathbf{1} - \mathbf{O}^{\parallel} = \mathbf{O}^{\perp} \tag{A.14}$$

B Matrix Elements of $\mathbf{G}^{(n)}$

The $\mathbf{G}^{(n)}$ matrix if Eq. (50) is divided into three spaces, O, V' and V'' . In the following we report the explicit expression for some relevant blocks of such matrix at different orders, according to Eq. (39), and following (33), (38) and (37).

$$\begin{aligned}
\mathbf{G}_{OV'}^{(0)} &= \mathbf{G}_{V'O}^{(0)\dagger} = \mathbf{C}_O^{(0)\dagger} (\underline{\mathbf{h}} + \underline{\mathbf{B}}[0]) \mathbf{C}_{V'}^{(0)} = 0 \\
\mathbf{G}_{OV''}^{(0)} &= \mathbf{G}_{V''O}^{(0)\dagger} = 0 \\
\mathbf{G}_{OV'}^{(1)} &= \mathbf{G}_{V'O}^{(1)\dagger} = \mathbf{C}_O^{(0)\dagger} \underline{\mathbf{B}}[\underline{1}] \mathbf{C}_{V'}^{(0)} = 0 \\
\mathbf{G}_{OV''}^{(1)} &= \mathbf{G}_{V''O}^{(1)\dagger} = \mathbf{C}_O^{(0)\dagger} \underline{\Omega}^{(1)} \mathbf{C}_{V''}^{(0)} \\
\mathbf{G}_{V'V''}^{(1)} &= \mathbf{G}_{V''V'}^{(1)\dagger} = \mathbf{C}_{V'}^{(0)\dagger} \underline{\Omega}^{(1)} \mathbf{C}_{V''}^{(0)} \\
\mathbf{G}_{OV'}^{(n)} &= \mathbf{G}_{V'O}^{(n)\dagger} = \mathbf{C}_O^{(0)\dagger} (\underline{\mathbf{B}}[\underline{n}] + n \underline{\mathbf{B}}[\overline{n-1}]) \mathbf{C}_{V'}^{(0)} \\
\mathbf{G}_{OV''}^{(n)} &= \mathbf{G}_{V''O}^{(n)\dagger} = n \mathbf{C}_O^{(0)\dagger} (\overline{\mathbf{B}}[\underline{n-1}] + (n-1) \overline{\mathbf{B}}[\overline{n-2}]) \mathbf{C}_{V''}^{(0)} \quad ; \quad \mathbf{G}_{OV''}^{(2)} = 0 \\
\mathbf{G}_{V'V''}^{(n)} &= \mathbf{G}_{V''V'}^{(n)\dagger} = n \mathbf{C}_{V'}^{(0)\dagger} (\overline{\mathbf{B}}[\underline{n-1}] + (n-1) \overline{\mathbf{B}}[\overline{n-2}]) \mathbf{C}_{V''}^{(0)} \quad ; \quad \mathbf{G}_{V'V''}^{(2)} = 0 \\
\mathbf{G}_{OO}^{(1)} &= \mathbf{G}_{OO}^{(1)\dagger} = \mathbf{C}_O^{(0)\dagger} \underline{\mathbf{B}}[\underline{1}] \mathbf{C}_O^{(0)} = 0 \\
\mathbf{G}_{V'V'}^{(1)} &= \mathbf{G}_{V'V'}^{(1)\dagger} = \mathbf{C}_{V'}^{(0)\dagger} \underline{\mathbf{B}}[\underline{1}] \mathbf{C}_{V'}^{(0)} = 0 \\
\mathbf{G}_{V''V''}^{(1)} &= \mathbf{G}_{V''V''}^{(1)\dagger} = \mathbf{C}_{V''}^{(0)\dagger} \underline{\mathbf{B}}[\underline{1}] \mathbf{C}_{V''}^{(0)} = 0 \\
\mathbf{G}_{OO}^{(2)} &= \mathbf{G}_{OO}^{(2)\dagger} = \mathbf{C}_O^{(0)\dagger} (\underline{\mathbf{B}}[\underline{2}] + 2 \underline{\mathbf{B}}[\overline{1}]) \mathbf{C}_O^{(0)} \\
\mathbf{G}_{V'V'}^{(2)} &= \mathbf{G}_{V'V'}^{(2)\dagger} = \mathbf{C}_{V'}^{(0)\dagger} (\underline{\mathbf{B}}[\underline{2}] + 2 \underline{\mathbf{B}}[\overline{1}]) \mathbf{C}_{V'}^{(0)} \\
\mathbf{G}_{V''V''}^{(2)} &= \mathbf{G}_{V''V''}^{(2)\dagger} = \mathbf{C}_{V''}^{(0)\dagger} (\underline{\mathbf{B}}[\underline{2}] + 2 \underline{\mathbf{B}}[\overline{1}]) \mathbf{C}_{V''}^{(0)}
\end{aligned} \tag{B.1}$$

As it turns out, a number of such blocks are null.

C Detailed derivation of energy contributions

Starting from Eq. (60) and following the expansion of the energy in Eq. (27), we can obtain energies at different perturbative orders. The zero-th order expression – Eq. (62) – is straightforward and corresponds to the total energy as obtained in the small basis.

The following trace relations, that can be derived from Equations (18), (19) and (29)–(31), will prove useful later on

$$Tr [\underline{\mathbf{B}}[n] \mathbf{D}^{(m)}] = Tr [\mathbf{B}[n] \underline{\mathbf{D}}^{(m)}] \quad (\text{C.1})$$

$$Tr [\overline{\mathbf{B}}[n] \mathbf{D}^{(m)}] = Tr [\mathbf{B}[n] \overline{\mathbf{D}}^{(m)}] \quad (\text{C.2})$$

$$Tr [\underline{\mathbf{B}}[\underline{n}] \mathbf{D}^{(m)}] = Tr [\underline{\mathbf{B}}[\underline{m}] \mathbf{D}^{(n)}] \quad (\text{C.3})$$

$$Tr [\underline{\mathbf{B}}[\overline{n}] \mathbf{D}^{(m)}] = Tr [\overline{\mathbf{B}}[\underline{m}] \mathbf{D}^{(n)}] \quad (\text{C.4})$$

$$Tr [\overline{\mathbf{B}}[\overline{n}] \mathbf{D}^{(m)}] = Tr [\overline{\mathbf{B}}[\overline{m}] \mathbf{D}^{(n)}] \quad (\text{C.5})$$

$$Tr [\boldsymbol{\Omega}^{(1)} \mathbf{D}^{(0)}] = 0 \quad (\text{C.6})$$

where we have used $[n]$ to indicate either $[\underline{n}]$ or $[\overline{n}]$.

Eq. (C.2), for example, is demonstrated by:

$$\begin{aligned} Tr [\overline{\mathbf{B}}[m] \mathbf{D}^{(n)}] &= Tr [\mathbf{O}^{\parallel\dagger} \mathbf{B}[m] \mathbf{O}^\perp \mathbf{D}^{(n)} + \mathbf{O}^{\perp\dagger} \mathbf{B}[m] \mathbf{O}^\parallel \mathbf{D}^{(n)}] \\ &= Tr [\mathbf{B}[m] \mathbf{O}^\perp \mathbf{D}^{(n)} \mathbf{O}^{\parallel\dagger} + \mathbf{B}[m] \mathbf{O}^\parallel \mathbf{D}^{(n)} \mathbf{O}^{\perp\dagger}] \\ &= Tr [\mathbf{B}[m] (\mathbf{O}^\perp \mathbf{D}^{(n)} \mathbf{O}^{\parallel\dagger} + \mathbf{O}^\parallel \mathbf{D}^{(n)} \mathbf{O}^{\perp\dagger})] = Tr [\mathbf{B}[m] \overline{\mathbf{D}}^{(n)}] \end{aligned} \quad (\text{C.7})$$

and analogolously for Eq. (C.1)

C.1 First order

The first-order energy is obtained by taking the first derivative $\partial E_{HF} \partial \lambda$ at $\lambda = 0$

$$E_{HF}^{(1)} = \left. \frac{\partial E_{HF}}{\partial \lambda} \right|_{\lambda=0} = \frac{1}{2} Tr [(\bar{\mathbf{h}} + \mathbf{F}^{(1)}) \mathbf{D}^{(0)} + (\underline{\mathbf{h}} + \mathbf{F}^{(0)}) \mathbf{D}^{(1)}] \quad (\text{C.8})$$

By inserting Eq. (38) in the above we obtain

$$\begin{aligned} E_{HF}^{(1)} &= \frac{1}{2} Tr [(\bar{\mathbf{h}} + \boldsymbol{\Omega}^{(1)} + \underline{\mathbf{B}}[\underline{1}]) \mathbf{D}^{(0)} + (2\underline{\mathbf{h}} + \underline{\mathbf{B}}[0]) \mathbf{D}^{(1)}] \\ &= \frac{1}{2} Tr [\underline{\mathbf{B}}[\underline{1}] \mathbf{D}^{(0)} + (2\underline{\mathbf{h}} + \underline{\mathbf{B}}[0]) \mathbf{D}^{(1)}] \\ &= Tr [\mathbf{F}^{(0)} \mathbf{D}^{(1)}] = 0 \end{aligned} \quad (\text{C.9})$$

The last line follows taking into account Eqs. (C.3), (C.6) and

$$Tr [\mathbf{F}^{(0)} \mathbf{D}^{(1)}] = Tr [\boldsymbol{\varepsilon}^{(0)} \mathbf{U}^{(1)} n + n \mathbf{U}^{(1)\dagger} \boldsymbol{\varepsilon}^{(0)}] = 0 \quad (\text{C.10})$$

which holds because $\boldsymbol{\varepsilon}^{(0)}$ is diagonal and the *occ-occ* block of $\mathbf{U}^{(1)}$ is zero.

C.2 Second order

let us differentiate once more the total energy with respect to λ , at $\lambda = 0$.

$$E_{HF}^{(2)} = \left. \frac{\partial^2 E_{HF}}{\partial \lambda^2} \right|_{\lambda=0} = \frac{1}{2} Tr [\mathbf{F}^{(2)} \mathbf{D}^{(0)} + 2(\bar{\mathbf{h}} + \mathbf{F}^{(1)}) \mathbf{D}^{(1)} + (\underline{\mathbf{h}} + \mathbf{F}^{(0)}) \mathbf{D}^{(2)}] \quad (\text{C.11})$$

This can be rewritten using (38) and (35) as:

$$E_{HF}^{(2)} = \frac{1}{2} Tr [(\underline{\mathbf{B}}[\underline{2}] + 2\bar{\underline{\mathbf{B}}}[\underline{1}] + 2\underline{\mathbf{B}}[\bar{1}]) \mathbf{D}^{(0)} + 2(\bar{\mathbf{h}} + \boldsymbol{\Omega}^{(1)} + \underline{\mathbf{B}}[\underline{1}]) \mathbf{D}^{(1)} + (2\underline{\mathbf{h}} + \underline{\mathbf{B}}[0]) \mathbf{D}^{(2)}] \quad (\text{C.12})$$

From Eqs. (C.3), (C.4) we have that $Tr[\underline{\mathbf{B}}[\underline{2}] \mathbf{D}^{(0)}] = Tr[\underline{\mathbf{B}}[0] \mathbf{D}^{(2)}]$, $Tr[\underline{\mathbf{B}}[\bar{1}] \mathbf{D}^{(0)}] = Tr[\bar{\underline{\mathbf{B}}}[0] \mathbf{D}^{(1)}]$ and $Tr[\bar{\underline{\mathbf{B}}}[\underline{1}] \mathbf{D}^{(0)}] = 0$. This leads to:

$$\begin{aligned}
E_{HF}^{(2)} &= \frac{1}{2} Tr \left[2 \left(2 \mathbf{\Omega}^{(1)} + \mathbf{B}[\underline{1}] \right) \mathbf{D}^{(1)} + 2 \left(\mathbf{h} + \mathbf{B}[0] \right) \mathbf{D}^{(2)} \right] \\
&= Tr \left[\mathbf{F}^{(1)} \mathbf{D}^{(1)} + \mathbf{F}^{(0)} \mathbf{D}^{(2)} + \mathbf{\Omega}^{(1)} \mathbf{D}^{(1)} \right]
\end{aligned} \tag{C.13}$$

We see that, for closed shells:

$$\begin{aligned}
Tr \left[\mathbf{F}^{(1)} \mathbf{D}^{(1)} \right] &= Tr \left[\mathbf{G}^{(1)} \mathbf{U}^{(1)} n + \mathbf{G}^{(1)} n \mathbf{U}^{(1)\dagger} \right] = 2 Tr \left[\mathbf{G}_{OV}^{(1)} \mathbf{U}_{VO}^{(1)} + \mathbf{G}_{VO}^{(1)} \mathbf{U}_{OV}^{(1)\dagger} \right] \\
&= 2 \sum_{ia} \left[\frac{G_{ia}^{(1)} G_{ai}^{(1)}}{\epsilon_i^{(0)} - \epsilon_a^{(0)}} - \frac{G_{ai}^{(1)} G_{ia}^{(1)}}{\epsilon_a^{(0)} - \epsilon_i^{(0)}} \right] = 4 \sum_{ia} U_{ai}^{(1)} U_{ia}^{(1)} (\epsilon_a^{(0)} - \epsilon_i^{(0)})
\end{aligned} \tag{C.14}$$

And, (also for closed shells):

$$\begin{aligned}
Tr \left[\mathbf{F}^{(0)} \mathbf{D}^{(2)} \right] &= Tr \left[\epsilon^{(0)} \mathbf{U}^{(2)} n + \epsilon^{(0)} n \mathbf{U}^{(2)\dagger} + 2 \epsilon^{(0)} \mathbf{U}^{(1)} n \mathbf{U}^{(1)\dagger} \right] \\
&= 2 Tr \left[\epsilon_O^{(0)} (\mathbf{U}_{OO}^{(2)} + \mathbf{U}_{OO}^{(2)\dagger}) + 2 \epsilon_V^{(0)} \mathbf{U}_{VO}^{(1)} \mathbf{U}_{OV}^{(1)\dagger} \right] \\
&= -4 Tr \left[\epsilon_O^{(0)} \mathbf{U}_{OV}^{(1)\dagger} \mathbf{U}_{VO}^{(1)} - \epsilon_V^{(0)} \mathbf{U}_{VO}^{(1)} \mathbf{U}_{OV}^{(1)\dagger} \right] \\
&= -4 \sum_{ia} U_{ai}^{(1)} U_{ia}^{(1)} (\epsilon_a^{(0)} - \epsilon_i^{(0)})
\end{aligned} \tag{C.15}$$

Where Eq. (49) was used. Finally, Eqs. (C.14) and (C.15) show that the first two terms in the last line of Eq. (C.13) cancel out each other leading to Eq. (64).

C.3 Third order

By further differentiating Eq. (27) we obtain

$$E_{HF}^{(3)} = \left. \frac{\partial^3 E_{HF}}{\partial \lambda^3} \right|_{\lambda=0} = \frac{1}{2} Tr \left[\mathbf{F}^{(3)} \mathbf{D}^{(0)} + 3 \mathbf{F}^{(2)} \mathbf{D}^{(1)} + 3 (\bar{\mathbf{h}} + \mathbf{F}^{(1)}) \mathbf{D}^{(2)} + (\mathbf{h} + \mathbf{F}^{(0)}) \mathbf{D}^{(3)} \right] \tag{C.16}$$

that can be written more explicitly using (38), (35), (36) as

$$E_{HF}^{(3)} = \frac{1}{2} Tr \left[(\underline{\mathbf{B}}[\underline{3}] + 3\overline{\mathbf{B}}[\underline{2}] + 3\underline{\mathbf{B}}[\overline{2}] + 6\overline{\mathbf{B}}[\overline{1}]) \mathbf{D}^{(0)} + 3 (\underline{\mathbf{B}}[\underline{2}] + 2\overline{\mathbf{B}}[\underline{1}] + 2\underline{\mathbf{B}}[\overline{1}]) \mathbf{D}^{(1)} \right. \\ \left. + 3 (\overline{\mathbf{h}} + \boldsymbol{\Omega}^{(1)} + \underline{\mathbf{B}}[\underline{1}]) \mathbf{D}^{(2)} + (2\underline{\mathbf{h}} + \underline{\mathbf{B}}[0]) \mathbf{D}^{(3)} \right] \quad (\text{C.17})$$

From Eqs. (C.3)–(C.5) we have that $Tr[\underline{\mathbf{B}}[\underline{3}] \mathbf{D}^{(0)}] = Tr[\underline{\mathbf{B}}[0] \mathbf{D}^{(3)}]$, $Tr[\underline{\mathbf{B}}[\overline{2}] \mathbf{D}^{(0)}] = Tr[\overline{\mathbf{B}}[0] \mathbf{D}^{(2)}]$, $Tr[\underline{\mathbf{B}}[\overline{1}] \mathbf{D}^{(1)}] = Tr[\overline{\mathbf{B}}[\underline{1}] \mathbf{D}^{(1)}]$ and $Tr[\overline{\mathbf{B}}[\underline{2}] \mathbf{D}^{(0)}] = 0$, $Tr[\overline{\mathbf{B}}[\overline{1}] \mathbf{D}^{(0)}] = 0$.

This leads to:

$$E_{HF}^{(3)} = \frac{1}{2} Tr \left[3 (\underline{\mathbf{B}}[\underline{2}] + 2\overline{\mathbf{B}}[\underline{1}] + 2\underline{\mathbf{B}}[\overline{1}]) \mathbf{D}^{(1)} + 3 (2\boldsymbol{\Omega}^{(1)} + \underline{\mathbf{B}}[\underline{1}]) \mathbf{D}^{(2)} + 2\mathbf{F}^{(0)} \mathbf{D}^{(3)} \right] \\ = \frac{1}{2} Tr \left[3\mathbf{F}^{(2)} \mathbf{D}^{(1)} + 3\mathbf{F}^{(1)} \mathbf{D}^{(2)} + 2\mathbf{F}^{(0)} \mathbf{D}^{(3)} + 3\boldsymbol{\Omega}^{(1)} \mathbf{D}^{(2)} \right] \quad (\text{C.18})$$

We see that:

$$Tr[\mathbf{F}^{(0)} \mathbf{D}^{(3)}] = Tr \left[\boldsymbol{\varepsilon}^{(0)} \mathbf{U}^{(3)} n + \boldsymbol{\varepsilon}^{(0)} n \mathbf{U}^{(3)\dagger} + 3\boldsymbol{\varepsilon}^{(0)} \mathbf{U}^{(2)} n \mathbf{U}^{(1)\dagger} + 3\boldsymbol{\varepsilon}^{(0)} \mathbf{U}^{(1)} n \mathbf{U}^{(2)\dagger} \right] \\ = 2Tr \left[\boldsymbol{\varepsilon}_O^{(0)} \mathbf{U}_{OO}^{(3)} + \boldsymbol{\varepsilon}_O^{(0)} \mathbf{U}_{OO}^{(3)\dagger} + 3\boldsymbol{\varepsilon}_V^{(0)} \mathbf{U}_{VO}^{(2)} \mathbf{U}_{OV}^{(1)\dagger} + 3\boldsymbol{\varepsilon}_V^{(0)} \mathbf{U}_{VO}^{(1)} \mathbf{U}_{OV}^{(2)\dagger} \right] \quad (\text{C.19})$$

From the derivatives of the orthonormality condition we get:

$$\mathbf{U}_{OO}^{(3)} + \mathbf{U}_{OO}^{(3)\dagger} = -3\mathbf{U}_{OV}^{(2)\dagger} \mathbf{U}_{VO}^{(1)} - 3\mathbf{U}_{OV}^{(1)\dagger} \mathbf{U}_{VO}^{(2)} \quad (\text{C.20})$$

which allows us to write

$$2Tr[\mathbf{F}^{(0)} \mathbf{D}^{(3)}] = -12 Tr \left[\boldsymbol{\varepsilon}_O^{(0)} \mathbf{U}_{OV}^{(2)\dagger} \mathbf{U}_{VO}^{(1)} + \boldsymbol{\varepsilon}_O^{(0)} \mathbf{U}_{OV}^{(1)\dagger} \mathbf{U}_{VO}^{(2)} - \boldsymbol{\varepsilon}_V^{(0)} \mathbf{U}_{VO}^{(2)} \mathbf{U}_{OV}^{(1)\dagger} - \boldsymbol{\varepsilon}_V^{(0)} \mathbf{U}_{VO}^{(1)} \mathbf{U}_{OV}^{(2)\dagger} \right] \\ = -12 Tr \left[\mathbf{U}_{OV}^{(2)\dagger} \left(\mathbf{U}_{VO}^{(1)} \boldsymbol{\varepsilon}_O^{(0)} - \boldsymbol{\varepsilon}_V^{(0)} \mathbf{U}_{VO}^{(1)} \right) + \left(\boldsymbol{\varepsilon}_O^{(0)} \mathbf{U}_{OV}^{(1)\dagger} - \mathbf{U}_{OV}^{(1)\dagger} \boldsymbol{\varepsilon}_V^{(0)} \right) \mathbf{U}_{VO}^{(2)} \right] \\ = -12 Tr \left[\mathbf{U}_{OV}^{(2)\dagger} \mathbf{G}_{VO}^{(1)} + \mathbf{G}_{OV}^{(1)} \mathbf{U}_{VO}^{(2)} \right] \quad (\text{C.21})$$

Moving on to the next term we write:

$$\begin{aligned}
Tr [\mathbf{F}^{(1)} \mathbf{D}^{(2)}] &= Tr \left[\mathbf{G}^{(1)} \mathbf{U}^{(2)} n + 2 \mathbf{G}^{(1)} \mathbf{U}^{(1)} n \mathbf{U}^{(1)\dagger} + \mathbf{G}^{(1)} n \mathbf{U}^{(2)\dagger} \right] \\
&= 2Tr \left[\mathbf{G}_{OO}^{(1)} \mathbf{U}_{OO}^{(2)} + \mathbf{G}_{OV}^{(1)} \mathbf{U}_{VO}^{(2)} + 2\mathbf{G}_{VV}^{(1)} \mathbf{U}_{VO}^{(1)} \mathbf{U}_{OV}^{(1)\dagger} + \mathbf{G}_{OO}^{(1)} \mathbf{U}_{OO}^{(2)\dagger} + \mathbf{G}_{VO}^{(1)} \mathbf{U}_{OV}^{(2)\dagger} \right]
\end{aligned} \tag{C.22}$$

where, by using Eq. (49), we obtain:

$$\begin{aligned}
3 Tr [\mathbf{F}^{(1)} \mathbf{D}^{(2)}] &= 6Tr \left[2\mathbf{G}_{VV}^{(1)} \mathbf{U}_{VO}^{(1)} \mathbf{U}_{OV}^{(1)\dagger} - 2\mathbf{G}_{OO}^{(1)} \mathbf{U}_{OV}^{(1)} \mathbf{U}_{VO}^{(1)\dagger} + \mathbf{G}_{OV}^{(1)} \mathbf{U}_{VO}^{(2)} + \mathbf{G}_{VO}^{(1)} \mathbf{U}_{OV}^{(2)\dagger} \right] \\
&= 6Tr \left[2 \mathbf{U}_{OV}^{(1)\dagger} \left(\mathbf{G}_{VV}^{(1)} \mathbf{U}_{VO}^{(1)} - \mathbf{U}_{VO}^{(1)} \mathbf{G}_{OO}^{(1)} \right) + \mathbf{G}_{OV}^{(1)} \mathbf{U}_{VO}^{(2)} + \mathbf{U}_{OV}^{(2)\dagger} \mathbf{G}_{VO}^{(1)} \right]
\end{aligned} \tag{C.23}$$

Now we move on to the next term

$$\begin{aligned}
3 Tr [\mathbf{F}^{(2)} \mathbf{D}^{(1)}] &= 3 Tr \left[\mathbf{G}^{(2)} \mathbf{U}^{(1)} n + \mathbf{G}^{(2)} n \mathbf{U}^{(1)\dagger} \right] = 6 Tr \left[\mathbf{G}_{OV}^{(2)} \mathbf{U}_{VO}^{(1)} + \mathbf{U}_{OV}^{(1)\dagger} \mathbf{G}_{VO}^{(2)} \right] \\
&= 6 Tr \left[\left(\mathbf{U}_{OV}^{(2)} \boldsymbol{\epsilon}_V^{(0)} - \boldsymbol{\epsilon}_O^{(0)} \mathbf{U}_{OV}^{(2)} + 2\mathbf{U}_{OV}^{(1)} \mathbf{G}_{VV}^{(1)} - 2\mathbf{G}_{OO}^{(1)} \mathbf{U}_{OV}^{(1)} \right) \mathbf{U}_{VO}^{(1)} \right. \\
&\quad \left. + \mathbf{U}_{OV}^{(1)\dagger} \left(\mathbf{U}_{VO}^{(2)} \boldsymbol{\epsilon}_O^{(0)} - \boldsymbol{\epsilon}_V \mathbf{U}_{VO}^{(2)} + 2\mathbf{U}_{VO}^{(1)} \mathbf{G}_{OO}^{(1)} - 2\mathbf{G}_{VV}^{(1)} \mathbf{U}_{VO}^{(1)} \right) \right]
\end{aligned} \tag{C.24}$$

Where we used Eq. (54).

Two useful substitutions can be made in the above:

$$\begin{aligned}
Tr \left[\left(\mathbf{U}_{OV}^{(2)} \boldsymbol{\epsilon}_V^{(0)} - \boldsymbol{\epsilon}_O^{(0)} \mathbf{U}_{OV}^{(2)} \right) \mathbf{U}_{VO}^{(1)} \right] &= \sum_{i,a} U_{ia}^{(2)} (\varepsilon_a - \varepsilon_i) U_{ai}^{(1)} = \sum_{i,a} U_{ia}^{(2)} (\varepsilon_a - \varepsilon_i) \frac{G_{ai}^{(1)}}{\varepsilon_i - \varepsilon_a} \\
&= -Tr \left[\mathbf{U}_{OV}^{(2)} \mathbf{G}_{VO}^{(1)} \right] = Tr \left[\mathbf{G}_{VO}^{(1)} \mathbf{U}_{OV}^{(2)\dagger} \right]
\end{aligned} \tag{C.25}$$

$$Tr \left[\left(\mathbf{U}_{VO}^{(2)} \boldsymbol{\epsilon}_O^{(0)} - \boldsymbol{\epsilon}_V \mathbf{U}_{VO}^{(2)} \right) \mathbf{U}_{OV}^{(1)\dagger} \right] = \sum_{i,a} U_{ai}^{(2)} (\varepsilon_i - \varepsilon_a) U_{ai}^{(1)} = \sum_{i,a} U_{ai}^{(2)} (\varepsilon_a - \varepsilon_i) \frac{G_{ai}^{(1)}}{\varepsilon_i - \varepsilon_a} = Tr \left[\mathbf{U}_{VO}^{(2)} \mathbf{G}_{OV}^{(1)} \right] \tag{C.26}$$

allowing us to write:

$$\begin{aligned}
3 \text{Tr} [\mathbf{F}^{(2)} \mathbf{D}^{(1)}] &= 6 \text{Tr} \left[\mathbf{G}_{VO}^{(1)} \mathbf{U}_{OV}^{(2)\dagger} + \mathbf{U}_{VO}^{(2)} \mathbf{G}_{OV}^{(1)} + \left(2\mathbf{U}_{OV}^{(1)} \mathbf{G}_{VV}^{(1)} - 2\mathbf{G}_{OO}^{(1)} \mathbf{U}_{OV}^{(1)} \right) \mathbf{U}_{VO}^{(1)} \right. \\
&\quad \left. + \mathbf{U}_{OV}^{(1)\dagger} \left(2\mathbf{U}_{VO}^{(1)} \mathbf{G}_{OO}^{(1)} - 2\mathbf{G}_{VV}^{(1)} \mathbf{U}_{VO}^{(1)} \right) \right] \\
&= 6 \text{Tr} \left[\mathbf{U}_{OV}^{(2)\dagger} \mathbf{G}_{VO}^{(1)} + \mathbf{G}_{OV}^{(1)} \mathbf{U}_{VO}^{(2)} - 4\mathbf{U}_{OV}^{(1)\dagger} \left(\mathbf{G}_{VV}^{(1)} \mathbf{U}_{VO}^{(1)} - \mathbf{U}_{VO}^{(1)} \mathbf{G}_{OO}^{(1)} \right) \right] \quad (C.27)
\end{aligned}$$

By substituting Eqs. (C.21), (C.23) and (C.27) in Eq. (C.17) the third order energy results in Eq. (65). Since the diagonal blocks of $\mathbf{G}^{(1)}$ are null – Eq. (B.1) – and that $\overline{\mathbf{D}}^{(2)} = \mathbf{0}$, as explained below Eq. (57), it follows that the third order contribution to the energy is null.

C.4 Fourth order

Taking the fourth order derivative of Eq. (27) we obtain:

$$\begin{aligned}
E_{HF}^{(4)} = \left. \frac{\partial^4 E_{HF}}{\partial \lambda^4} \right|_{\lambda=0} &= \frac{1}{2} \text{Tr} \left[\mathbf{F}^{(4)} \mathbf{D}^{(0)} + 4\mathbf{F}^{(3)} \mathbf{D}^{(1)} \right. \\
&\quad \left. + 6\mathbf{F}^{(2)} \mathbf{D}^{(2)} + 4(\mathbf{h}^{(1)} + \mathbf{F}^{(1)}) \mathbf{D}^{(3)} \right. \\
&\quad \left. + (\mathbf{h}^{(0)} + \mathbf{F}^{(0)}) \mathbf{D}^{(4)} \right] \quad (C.28)
\end{aligned}$$

That is expanded, by virtue of (38), (35), (36) and (37) into

$$\begin{aligned}
E_{HF}^{(4)} &= \frac{1}{2} \text{Tr} \left[(\underline{\mathbf{B}}[\underline{4}] + 4\overline{\mathbf{B}}[\underline{3}] + 4\underline{\mathbf{B}}[\overline{3}] + 12\overline{\mathbf{B}}[\overline{2}]) \mathbf{D}^{(0)} + 4(\underline{\mathbf{B}}[\underline{3}] + 3\overline{\mathbf{B}}[\underline{2}] + 3\underline{\mathbf{B}}[\overline{2}] + 6\overline{\mathbf{B}}[\overline{1}]) \mathbf{D}^{(1)} \right. \\
&\quad \left. + 6(\underline{\mathbf{B}}[\underline{2}] + 2\overline{\mathbf{B}}[\underline{1}] + 2\underline{\mathbf{B}}[\overline{1}]) \mathbf{D}^{(2)} + 4(\overline{\mathbf{h}} + \boldsymbol{\Omega}^{(1)} + \underline{\mathbf{B}}[\underline{1}]) \mathbf{D}^{(3)} + (2\underline{\mathbf{h}} + \underline{\mathbf{B}}^{(0)}) \mathbf{D}^{(4)} \right] \quad (C.29)
\end{aligned}$$

From Eqs. (C.3)–(C.5) we have that $Tr[\underline{\mathbf{B}}[\underline{4}] \mathbf{D}^{(0)}] = Tr[\underline{\mathbf{B}}[\underline{0}] \mathbf{D}^{(4)}]$, $Tr[\underline{\mathbf{B}}[\underline{3}] \mathbf{D}^{(0)}] = Tr[\underline{\mathbf{B}}[\underline{0}] \mathbf{D}^{(3)}]$, and $Tr[\underline{\mathbf{B}}[\underline{3}] \mathbf{D}^{(0)}] = 0$, $Tr[\underline{\mathbf{B}}[\underline{2}] \mathbf{D}^{(0)}] = 0$.

This leads to:

$$\begin{aligned}
E_{HF}^{(4)} &= \frac{1}{2} Tr \left[4 \left(\underline{\mathbf{B}}[\underline{3}] + 3\underline{\mathbf{B}}[\underline{2}] + 3\underline{\mathbf{B}}[\underline{2}] + 6\underline{\mathbf{B}}[\underline{1}] \right) \mathbf{D}^{(1)} \right. \\
&\quad \left. + 6 \left(\underline{\mathbf{B}}[\underline{2}] + 2\underline{\mathbf{B}}[\underline{1}] + 2\underline{\mathbf{B}}[\underline{1}] \right) \mathbf{D}^{(2)} + 4 \left(2\underline{\Omega}^{(1)} + \underline{\mathbf{B}}[\underline{1}] \right) \mathbf{D}^{(3)} + 2(\underline{\mathbf{h}} + \underline{\mathbf{B}}[\underline{0}]) \mathbf{D}^{(4)} \right] \\
&= \frac{1}{2} Tr \left[24 \underline{\mathbf{B}}[\underline{1}] \mathbf{D}^{(1)} + 6 \left(\underline{\mathbf{B}}[\underline{2}] + 4\underline{\mathbf{B}}[\underline{1}] + 4\underline{\mathbf{B}}[\underline{1}] \right) \mathbf{D}^{(2)} \right. \\
&\quad \left. + 8 \left(\underline{\Omega}^{(1)} + \underline{\mathbf{B}}[\underline{1}] \right) \mathbf{D}^{(3)} + 2(\underline{\mathbf{h}} + \underline{\mathbf{B}}[\underline{0}]) \mathbf{D}^{(4)} \right] \\
&= Tr \left[3\mathbf{F}^{(2)} \mathbf{D}^{(2)} + 4\mathbf{F}^{(1)} \mathbf{D}^{(3)} + \mathbf{F}^{(0)} \mathbf{D}^{(4)} + 6 \left(\underline{\mathbf{B}}[\underline{1}] + \underline{\mathbf{B}}[\underline{1}] \right) \mathbf{D}^{(2)} + 12 \underline{\mathbf{B}}[\underline{1}] \mathbf{D}^{(1)} \right] \quad (\text{C.30})
\end{aligned}$$

Where we used $Tr[\underline{\mathbf{B}}[\underline{3}] \mathbf{D}^{(1)}] = Tr[\underline{\mathbf{B}}[\underline{1}] \mathbf{D}^{(3)}]$, $Tr[\underline{\mathbf{B}}[\underline{2}] \mathbf{D}^{(1)}] = Tr[\underline{\mathbf{B}}[\underline{1}] \mathbf{D}^{(2)}]$, $Tr[\underline{\mathbf{B}}[\underline{2}] \mathbf{D}^{(1)}] = Tr[\underline{\mathbf{B}}[\underline{1}] \mathbf{D}^{(2)}]$

We see, then, that:

$$\begin{aligned}
Tr[\mathbf{F}^{(0)} \mathbf{D}^{(4)}] &= Tr \left[\underline{\epsilon}^{(0)} \mathbf{U}^{(4)} n + \underline{\epsilon}^{(0)} n \mathbf{U}^{(4)\dagger} + 4\underline{\epsilon}^{(0)} \mathbf{U}^{(3)} n \mathbf{U}^{(1)\dagger} + 6\underline{\epsilon}^{(0)} \mathbf{U}^{(2)} n \mathbf{U}^{(2)\dagger} + 4\underline{\epsilon}^{(0)} \mathbf{U}^{(1)} n \mathbf{U}^{(3)\dagger} \right] \\
&= 2Tr \left[\underline{\epsilon}_O^{(0)} \mathbf{U}_{OO}^{(4)} + \underline{\epsilon}_O^{(0)} \mathbf{U}_{OO}^{(4)\dagger} + 4\underline{\epsilon}_V^{(0)} \mathbf{U}_{VO}^{(3)} \mathbf{U}_{OV}^{(1)\dagger} \right. \\
&\quad \left. + 6\underline{\epsilon}_V^{(0)} \mathbf{U}_{VO}^{(2)} \mathbf{U}_{OV}^{(2)\dagger} + 6\underline{\epsilon}_O^{(0)} \mathbf{U}_{OO}^{(2)} \mathbf{U}_{OO}^{(2)\dagger} + 4\underline{\epsilon}_V^{(0)} \mathbf{U}_{VO}^{(1)} \mathbf{U}_{OV}^{(3)\dagger} \right] \quad (\text{C.31})
\end{aligned}$$

From the orthonormality condition:

$$\mathbf{U}_{OO}^{(4)} + \mathbf{U}_{OO}^{(4)\dagger} = -4\mathbf{U}_{OV}^{(3)\dagger} \mathbf{U}_{VO}^{(1)} - 6 \left(\mathbf{U}_{OV}^{(2)\dagger} \mathbf{U}_{VO}^{(2)} + \mathbf{U}_{OO}^{(2)\dagger} \mathbf{U}_{OO}^{(2)} \right) - 4\mathbf{U}_{OV}^{(1)\dagger} \mathbf{U}_{VO}^{(3)} \quad (\text{C.32})$$

Then,

$$\begin{aligned}
Tr [\mathbf{F}^{(0)} \mathbf{D}^{(4)}] &= -4 Tr \left[2 \mathbf{U}_{OV}^{(3)\dagger} \left(\mathbf{U}_{VO}^{(1)} \boldsymbol{\varepsilon}_O^{(0)} - \boldsymbol{\varepsilon}_V^{(0)} \mathbf{U}_{VO}^{(1)} \right) - 2 \left(\mathbf{U}_{OV}^{(1)\dagger} \boldsymbol{\varepsilon}_V^{(0)} - \boldsymbol{\varepsilon}_O^{(0)} \mathbf{U}_{OV}^{(1)\dagger} \right) \mathbf{U}_{VO}^{(3)} \right. \\
&\quad \left. + 3 \left(\mathbf{U}_{VO}^{(2)} \boldsymbol{\varepsilon}_O^{(0)} - \boldsymbol{\varepsilon}_V^{(0)} \mathbf{U}_{VO}^{(2)} \right) \mathbf{U}_{OV}^{(2)\dagger} + 3 \mathbf{U}_{OO}^{(2)\dagger} \left(\mathbf{U}_{OO}^{(2)} \boldsymbol{\varepsilon}_O^{(0)} - \boldsymbol{\varepsilon}_O^{(0)} \mathbf{U}_{OO}^{(2)} \right) \right] \\
&= -4 Tr \left[2 \left(\mathbf{U}_{OV}^{(3)\dagger} \mathbf{G}_{VO}^{(1)} + \mathbf{G}_{OV}^{(1)} \mathbf{U}_{VO}^{(3)} \right) \right. \\
&\quad \left. + 3 \mathbf{U}_{OV}^{(2)\dagger} \left(\mathbf{G}_{VO}^{(2)} + 2 \mathbf{G}_{VV}^{(1)} \mathbf{U}_{VO}^{(1)} - 2 \mathbf{U}_{VO}^{(1)} \mathbf{G}_{OO}^{(1)} \right) + 3 \mathbf{U}_{OO}^{(2)\dagger} \left(\mathbf{G}_{OO}^{(2)} + 2 \mathbf{G}_{OV}^{(1)} \mathbf{U}_{VO}^{(1)} - \boldsymbol{\varepsilon}_{OO}^{(2)} \right) \right]
\end{aligned} \tag{C.33}$$

Let us continue with:

$$\begin{aligned}
4 Tr [\mathbf{F}^{(1)} \mathbf{D}^{(3)}] &= 8 Tr \left[\mathbf{G}_{OO}^{(1)} \mathbf{U}_{OO}^{(3)} + \mathbf{G}_{OV}^{(1)} \mathbf{U}_{VO}^{(3)} + 3 \mathbf{G}_{VO}^{(1)} \mathbf{U}_{OO}^{(2)} \mathbf{U}_{OV}^{(1)\dagger} \right. \\
&\quad \left. + 3 \mathbf{G}_{VV}^{(1)} \mathbf{U}_{VO}^{(2)} \mathbf{U}_{OV}^{(1)\dagger} + 3 \mathbf{G}_{VV}^{(1)} \mathbf{U}_{VO}^{(1)} \mathbf{U}_{OV}^{(2)\dagger} \right. \\
&\quad \left. + 3 \mathbf{G}_{OV}^{(1)} \mathbf{U}_{VO}^{(1)} \mathbf{U}_{OO}^{(2)\dagger} + \mathbf{G}_{OO}^{(1)} \mathbf{U}_{OO}^{(3)\dagger} + \mathbf{G}_{VO}^{(1)} \mathbf{U}_{OV}^{(3)\dagger} \right] \\
&= 8 Tr \left[-3 \mathbf{G}_{OO}^{(1)} \left(\mathbf{U}_{OV}^{(2)\dagger} \mathbf{U}_{VO}^{(1)} + \mathbf{U}_{OV}^{(1)\dagger} \mathbf{U}_{VO}^{(2)} \right) + \left(\mathbf{G}_{OV}^{(1)} \mathbf{U}_{VO}^{(3)} + \mathbf{G}_{VO}^{(1)} \mathbf{U}_{OV}^{(3)\dagger} \right) \right. \\
&\quad \left. + 3 \mathbf{G}_{VO}^{(1)} \mathbf{U}_{OO}^{(2)} \mathbf{U}_{OV}^{(1)\dagger} + 3 \mathbf{G}_{VV}^{(1)} \mathbf{U}_{VO}^{(2)} \mathbf{U}_{OV}^{(1)\dagger} \right. \\
&\quad \left. + 3 \mathbf{G}_{VV}^{(1)} \mathbf{U}_{VO}^{(1)} \mathbf{U}_{OV}^{(2)\dagger} + 3 \mathbf{G}_{OV}^{(1)} \mathbf{U}_{VO}^{(1)} \mathbf{U}_{OO}^{(2)\dagger} \right]
\end{aligned} \tag{C.34}$$

where in the last step we used Eq. (C.20). Combining Eqs. (C.33) and (C.34) we obtain:

$$\begin{aligned}
4 Tr [\mathbf{F}^{(1)} \mathbf{D}^{(3)}] + Tr [\mathbf{F}^{(0)} \mathbf{D}^{(4)}] &= 12 Tr \left[\mathbf{U}_{OO}^{(2)\dagger} \left(\boldsymbol{\varepsilon}_{OO}^{(2)} - \mathbf{G}_{OO}^{(2)} \right) - \mathbf{U}_{OV}^{(2)\dagger} \mathbf{G}_{VO}^{(2)} \right. \\
&\quad \left. + 2 \mathbf{U}_{VO}^{(2)} \left(\mathbf{U}_{OV}^{(1)\dagger} \mathbf{G}_{VV}^{(1)} - \mathbf{G}_{OO}^{(1)} \mathbf{U}_{OV}^{(1)\dagger} \right) + 2 \mathbf{U}_{OO}^{(2)} \mathbf{U}_{OV}^{(1)\dagger} \mathbf{G}_{VO}^{(1)} \right]
\end{aligned} \tag{C.35}$$

Then, combining with

$$3 \operatorname{Tr} [\mathbf{F}^{(2)} \mathbf{D}^{(2)}] = 6 \operatorname{Tr} \left[\mathbf{G}_{OO}^{(2)} \left(\mathbf{U}_{OO}^{(2)} + \mathbf{U}_{OO}^{(2)\dagger} \right) + \mathbf{G}_{OV}^{(2)} \mathbf{U}_{VO}^{(2)} + \mathbf{U}_{OV}^{(2)\dagger} \mathbf{G}_{VO}^{(2)} + 2 \mathbf{G}_{VV}^{(2)} \mathbf{U}_{VO}^{(1)} \mathbf{U}_{OV}^{(1)\dagger} \right] \quad (\text{C.36})$$

We obtain:

$$\begin{aligned} E_{HF}^{(4)} = & 12 \operatorname{Tr} \left[\mathbf{U}_{OO}^{(2)\dagger} \boldsymbol{\varepsilon}_{OO}^{(2)} + \mathbf{G}_{VV}^{(2)} \mathbf{U}_{VO}^{(1)} \mathbf{U}_{OV}^{(1)\dagger} \right. \\ & \left. + 2 \mathbf{U}_{VO}^{(2)} \left(\mathbf{U}_{OV}^{(1)\dagger} \mathbf{G}_{VV}^{(1)} - \mathbf{G}_{OO}^{(1)} \mathbf{U}_{OV}^{(1)\dagger} \right) + 2 \mathbf{G}_{VO}^{(1)} \mathbf{U}_{OO}^{(2)} \mathbf{U}_{OV}^{(1)\dagger} + \frac{1}{2} \left(\overline{\mathbf{B}}[\underline{1}] + \underline{\mathbf{B}}[\overline{1}] \right) \mathbf{D}^{(2)} \right] \end{aligned} \quad (\text{C.37})$$

By exploiting Eq. (49), assuming Hermiticity of $\mathbf{U}_{OO}^{(2)\dagger}$ and using the fact that $E^{(4)}$ is real, we get our final expression for the fourth-order energy reported in Eq. (66)

References

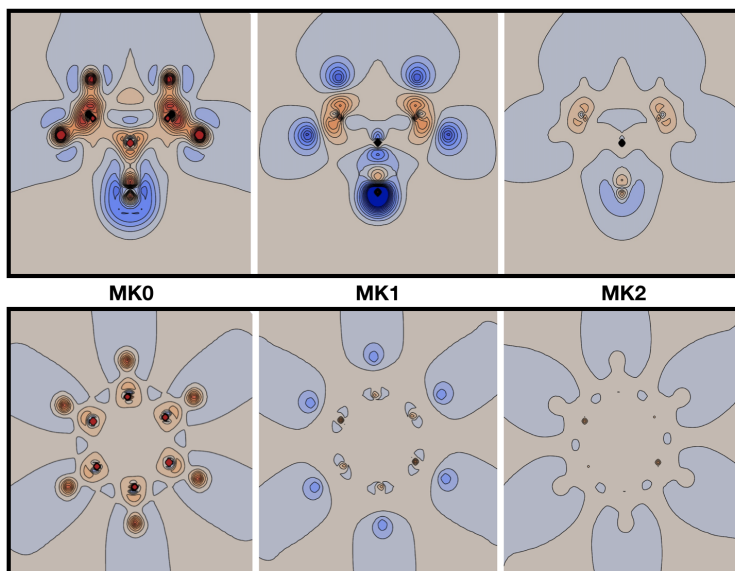
- (1) Jurgens-Lutovsky, R.; Almlöf, J. Dual Basis Sets in Calculations of Electron Correlation. *Chem. Phys. Lett.* **1991**, *178*, 451.
- (2) Havriliak, S.; King, H. F. Rydberg radicals. 1. Frozen-core model for Rydberg levels of the ammonium radical. *J. Am. Chem. Soc.* **1983**, *105*, 4–12.
- (3) Havriliak, S.; Furlani, T. R.; King, H. F. Rydberg levels of the sodium atom and the ammonium radical calculated by perturbation theory. *Can. J. Phys.* **1984**, *62*, 1336–1346.
- (4) Wolinski, K.; Pulay, P. Second-order Møller–Plesset calculations with dual basis sets. *J. Chem. Phys.* **2003**, *118*, 9497–9503.

- (5) Pulay, P.; Saebø, S. Orbital-invariant formulation and second-order gradient evaluation in Møller-Plesset perturbation theory. *Theor. Chem. Acc.* **1986**, *69*, 357–368.
- (6) Liang, W.; Head-Gordon, M. Approaching the basis set limit in density functional theory calculations using dual basis sets without diagonalization. *J. Phys. Chem. A* **2004**, *108*, 3206–3210.
- (7) Steele, R. P.; Shao, Y.; DiStasio, R. A.; Head-Gordon, M. Dual-Basis Analytic Gradients. 1. Self-Consistent Field Theory. *J. Phys. Chem. A* **2006**, *110*, 13915–13922.
- (8) Steele, R.; DiStasio, R. A.; Shao, Y.; Kong, J.; Head-Gordon, M. Dual-basis second-order Møller-Plesset perturbation theory: A reduced-cost reference for correlation calculations. *J. Chem. Phys.* **2006**, *125*, 074108.
- (9) Steele, R. P.; Head-Gordon, M.; Tully, J. C. Ab Initio Molecular Dynamics with Dual Basis Set Methods. *J. Phys. Chem. A* **2010**, *114*, 11853–11860.
- (10) Nakajima, T.; Hirao, K. A dual-level approach to density-functional theory. *J. Chem. Phys.* **2006**, *124*, 184108.
- (11) Deng, J.; Gilbert, A.; Gill, P. Density functional triple jumping. *Phys. Chem. Chem. Phys.* **2010**, *12*, 10759–10765.
- (12) Deng, J.; Gill, P. A new approach to dual-basis second-order Møller-Plesset calculations. *J. Chem. Phys.* **2011**, *134*, 081103.
- (13) Røeggen, I.; Gao, B. Perturbed atoms in molecules and solids: The PATMOS model. *J. Chem. Phys.* **2013**, *139*, 094104.
- (14) Røeggen, I.; Gao, B. Combination of large and small basis sets in electronic structure calculations on large systems. *J. Chem. Phys.* **2018**, *148*, 134118.

- (15) Ferrero, M.; Rérat, M.; Kirtman, B.; Dovesi, R. Calculation of first and second static hyperpolarizabilities of one-to three-dimensional periodic compounds. Implementation in the CRYSTAL code. *J. Chem. Phys.* **2008**, *129*, 244110.
- (16) Maschio, L.; Rérat, M.; Kirtman, B.; Dovesi, R. Calculation of the dynamic first electronic hyperpolarizability $\beta(-\omega_\sigma; \omega_1, \omega_2)$ of periodic systems. Theory, validation, and application to multi-layer MoS₂. *J. Chem. Phys.* **2015**, *143*, 244102.
- (17) Maschio, L.; Kirtman, B.; Orlando, R.; Rérat, M. *Ab Initio* Analytical Infrared Intensities for Periodic Systems through a Coupled Perturbed Hartree-Fock/Kohn-Sham method. *J. Chem. Phys.* **2012**, *137*, 204113.
- (18) Maschio, L.; Kirtman, B.; Rérat, M.; Orlando, R.; Dovesi, R. Ab initio analytical Raman intensities for periodic systems through a coupled perturbed Hartree-Fock/Kohn-Sham method in an atomic orbital basis. I. Theory. *J. Chem. Phys.* **2013**, *139*, 164101.
- (19) Maschio, L.; Kirtman, B.; Rérat, M.; Orlando, R.; Dovesi, R. Ab initio analytical Raman intensities for periodic systems through a coupled perturbed Hartree-Fock/Kohn-Sham method in an atomic orbital basis. II. Validation and comparison with experiments. *J. Chem. Phys.* **2013**, *139*, 164102.
- (20) Ewald, P. P. Die Berechnung optischer und elektrostatischer Gitterpotentiale. *Ann. Phys.* **1921**, *369*, 253–287.
- (21) Saunders, V.; Freyria-Fava, C.; Dovesi, R.; Salasco, L.; Roetti, C. On the electrostatic potential in crystalline systems where the charge density is expanded in Gaussian functions. *Mol. Phys.* **1992**, *77*, 629–665.
- (22) Dalgarno, A.; Stewart, A. On the perturbation theory of small disturbances. *Proc. R. Soc. Londoni, Ser. A* **1956**, *238*, 269–275.

- (23) Dalgarno, A.; Stewart, A. A perturbation calculation of properties of the $2\text{ p}\pi$ state of HeH_2^+ . *Proc. R. Soc. London, Ser. A* **1957**, *240*, 274–283.
- (24) Dalgarno, A.; Stewart, A. A perturbation calculation of properties of the helium iso-electronic sequence. *Proc. R. Soc. London, Ser. A* **1958**, *247*, 245–259.
- (25) Tuan, D. F. General Expression for the Interchange Theorem of Double Perturbation Theory. *J. Chem. Phys.* **1967**, *46*, 2435–2438.
- (26) Hirschfelder, J. O.; Brown, W. B.; Epstein, S. T. Recent developments in perturbation theory. *Adv. Quantum Chem.* **1964**, *1*, 255 – 374.
- (27) Karna, S. P.; Dupuis, M. Frequency dependent nonlinear optical properties of molecules: Formulation and implementation in the HONDO program. *J. Comput. Chem.* **1991**, *12*, 487–504.
- (28) Pisani, C.; Busso, M.; Capecchi, G.; Casassa, S.; Dovesi, R.; Maschio, L.; Zicovich-Wilson, C.; Schütz, M. Local-MP2 electron correlation method for nonconducting crystals. *J. Chem. Phys.* **2005**, *122*, 094133.
- (29) Note that the projection matrices are transposed as compared to Eq.(A.6). That is because the density matrix is defined as $\mathbf{C} n \mathbf{C}^\dagger$.
- (30) Aitken, A. C. On Bernoulli’s Numerical Solution of Algebraic Equations. *Proc. R. Soc. Edinburgh* **1927**, *46*, 289–305.
- (31) Weniger, E. J.; Kirtman, B. Extrapolation methods for improving the convergence of oligomer calculations to the infinite chain limit of quasi-one-dimensional stereoregular polymers. *Comput. Math. Appl.* **2003**, *45*, 189–215.
- (32) Pople, J. A.; Gill, P.; Johnson, B. G. Kohn—Sham density-functional theory within a finite basis set. *Chem. Phys. Lett.* **1992**, *199*, 557.

- (33) Johnson, B. G.; Frisch, M. J. An implementation of analytic second derivatives of the gradient-corrected density functional energy. *J. Chem. Phys.* **1994**, *100*, 7429–7442.
- (34) Orlando, R.; Lacivita, V.; Bast, R.; Ruud, K. Calculation of the first static hyperpolarizability tensor of three-dimensional periodic compounds with a local basis set: A comparison of LDA, PBE, PBE0, B3LYP, and HF results. *J. Chem. Phys.* **2010**, *132*, 244106.
- (35) Dovesi, R.; Erba, A.; Orlando, R.; Zicovich-Wilson, C. M.; Civalleri, B.; Maschio, L.; Rérat, M.; Casassa, S.; Baima, J.; Salustro, S.; Kirtman, B. Quantum-mechanical condensed matter simulations with CRYSTAL. *Wiley Interdiscip. Rev.: Comput. Mol. Sci* **2018**, *8*, e1360.
- (36) Pulay, P. Improved SCF convergence acceleration. *J. Comput. Chem.* **1982**, *3*, 556–560.
- (37) Maschio, L. Direct inversion of the iterative subspace (DIIS) convergence accelerator for crystalline solids employing Gaussian basis sets. *Theor. Chem. Acc.* **2018**, *137*, 60.
- (38) Ekström, U.; Visscher, L.; Bast, R.; Thorvaldsen, A. J.; Ruud, K. Arbitrary-order density functional response theory from automatic differentiation. *J. Chem. Theory Comput.* **2010**, *6*, 1971–1980.
- (39) Beata, G.; Perego, G.; Civalleri, B. CRYSPLOT: A new tool to visualize physical and chemical properties of molecules, polymers, surfaces, and crystalline solids. *J. Comput. Chem.* **2019**, *40*, 2329.
- (40) Steele, R. P.; Head-Gordon, M. Dual-basis self-consistent field methods: 6-31G* calculations with a minimal 6-4G primary basis. *Mol. Phys.* **2007**, *105*, 2455–2473.
- (41) Helgaker, T.; Jørgensen, P.; Olsen, J. *Molecular Electronic Structure Theory*; John Wiley and Sons: Chichester, UK, 2000.



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