

1 Research Project Objectives

Exploring most of the biological phenomena at molecular level requires detailed simulations of relatively large molecular frameworks or networks. Unfortunately, indispensable treatment of quantum effects that rule intermolecular interactions and molecular conformations is often a major obstacle for simulations due to prohibitively large number of electrons and complexity of emerging theories. Although the existing available approximate schemes, from the *continuum* representation of the environment¹ through the fragment-based methods² with explicit embedding^{3,4} enable modelling broad categories of bulk liquid systems and macromolecules, they often face certain limitations due to the following two reasons: (1) high level electron correlation is computationally very expensive to treat electronic states in extended systems in *ab initio* manner; (2) *ab initio* vibrational analyses of extended systems are prohibitively difficult.

For example, studying electronic couplings at short distances and associated excitation energy transfer (EET) processes^{5,6} is challenging because the usually large size of electronic chromophores prevents from treating the entire molecular aggregate by methods that include necessary amount of electron correlation to describe electronically excited states. Particularly important here is the couplings between chlorophyll subunits in special pairs of reaction centres in photosystems, within which the energy transfer is still not fully understood.⁶

Another intriguing problem is explaining the origins of life on Earth that requires investigating the photostability of electronically excited states of nucleic acid precursors in the case of which electron correlation has to be taken into account at relatively high level of theory while including solvent and all the associated intermolecular interactions at the same time. Nowadays, incorporation of explicit solvent molecules in *ab initio* calculations performed in such studies is often limited to several species^{7,8} which might be not enough to get accurate thermodynamics and kinetics.

Describing molecular vibrations under the influence of environment is yet another problem that is not fully resolved yet,^{9,10} though it is of customary importance in studying the sub-nanosecond dynamics of macromolecules in terms of the vibrational spectroscopy,¹¹ because ultrafast conformational flexibility of many proteins and nucleic acids is a key to understand their functions.^{12,13}

Therefore, to take into account surroundings, simplistic assumptions are made frequently (for example, Pauli repulsion between QM level and environment is neglected leading to electrostatic embedding schemes³). However, it is relevant to develop new simple but yet accurate and computationally efficient technique that offers solutions in a preferably ‘unified’ way to the problems mentioned above.

One of the goals of this project is to generalize the effective one-electron potentials technique used previously^{14–17} to simplify the rigorous and costly quantum chemistry models of extended systems with a particular emphasis on solvation and EET. Electron repulsion integrals (ERI’s), which are oftentimes the main bottleneck in simulating large systems, are projected out from the working equations to **ultimately form the effective one-electron functions** that are much easier to handle. The proposed approach follows the notion of the importance of one-electron densities in chemistry,¹⁶ thus reducing the complicated summations involving ERI’s to much shorter expressions involving only one-electron integrals. It is believed that the proposed concept can be helpful in designing future methods tuned for studying electronically excited states in solutions, better describing molecular dynamics as well as enabling the vibrational analysis of extended systems at high levels of theory. In particular, the above techniques could be adopted in the electron density-based interaction energy decomposition scheme recently developed by Mandado and Hermida-Ramón¹⁸ which can address arbitrary level of theory. This would enable the development of a novel fragment-based methodology similar to the commonly used effective fragment potential (EFP) method^{19,20} but derived at post-Hartree–Fock wave function level, which would find applications in the vibrational and electronic solvatochromism, photochemistry of nucleobase precursors and non-adiabatic molecular dynamics in

condensed phases, areas largely unexplored due to excessive computational demands.

2 Significance of the Project

It is desirable to construct a robust, effective and accurate method of describing the energetics and other properties of extended systems at correlated level of theory. However, state-of-the-art EFP-based approaches, which are quite accurate and fast, are limited only to ground state Hartree–Fock or Kohn–Sham single Slater determinants.^{19–21} Treatment of electronically excited states is only achievable through QM/EFP or similar schemes which are based on polarization embedding at the present time.^{3,22} Moreover, EFP-related schemes require semi-empirical treatment of charge-penetration effects due to extensive use of multipole expansions. It is believed that the OEP’s introduced in this Proposal would enable the development of electron density-based (not energy-based) generalized effective fragment potential scheme that is not limited to Hartree–Fock level and includes the exchange-repulsion, polarization and dispersion effects at the electron correlation level as well. This in turn would enable fast and accurate computations of many specific properties of molecular aggregates, including solvent effects on energetics and dynamics of electronically excited states.

In summary, the proposed technique could be efficiently combined with the existing methods of quantum chemistry. Therefore, due to the fundamental meaning of the one-electron potentials they could be applicable in many diverse fields of molecular biology and physical chemistry.

3 Work Plan

The work plan is depicted in Figure 1 on page 3. In the planned research, the *ab initio* effective potential functions are formulated for the three fundamental aspects:

- I. the electron-hole transfer (ET/HT) mechanism in the EET process,
- II. the Pauli repulsion between two molecules, and
- III. the electronic density distortion due to environment.

The tasks are planned to be undertaken in a group of 4 researchers (including the Project Leader and excluding the Research Partner) working mostly on implementations of newly derived equations that are sketched in Section 4. Project I (ET/HT mechanisms in EET) is independent of other projects. However, the development of OEP’s in Project I will be closely similar to works within Project II (Pauli repulsion potentials) because analogous procedures will be used. Projects II and III (polarization deformation densities) are independent of each other as well. It is planned that each project will be summarized with one publication in international journal such as *The Journal of Chemical Physics*, *Journal of Chemical Theory and Computation* and others. Note that numbers of these Projects are neither correlated with their importance nor turn in which they should be carried out.

4 Research Methodology

4.1 The Concept of Generalized Effective One-Electron Potentials

In this Section, the effective one-electron potentials (OEP’s) are defined. In brief, the main principle is to rewrite the arbitrary function f as*

$$f[(\phi_i^A \phi_j^A | \phi_k^B \phi_l^B)] = (\phi_i^A | v_{kl}^B | \phi_j^A) \rightarrow \text{point charge or density fitting} \quad (1a)$$

* The following notation of ERI’s is used herein: $(\phi_i \phi_j | \phi_k \phi_l) \equiv \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1) \phi_j(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_k^*(\mathbf{r}_2) \phi_l(\mathbf{r}_2)$.

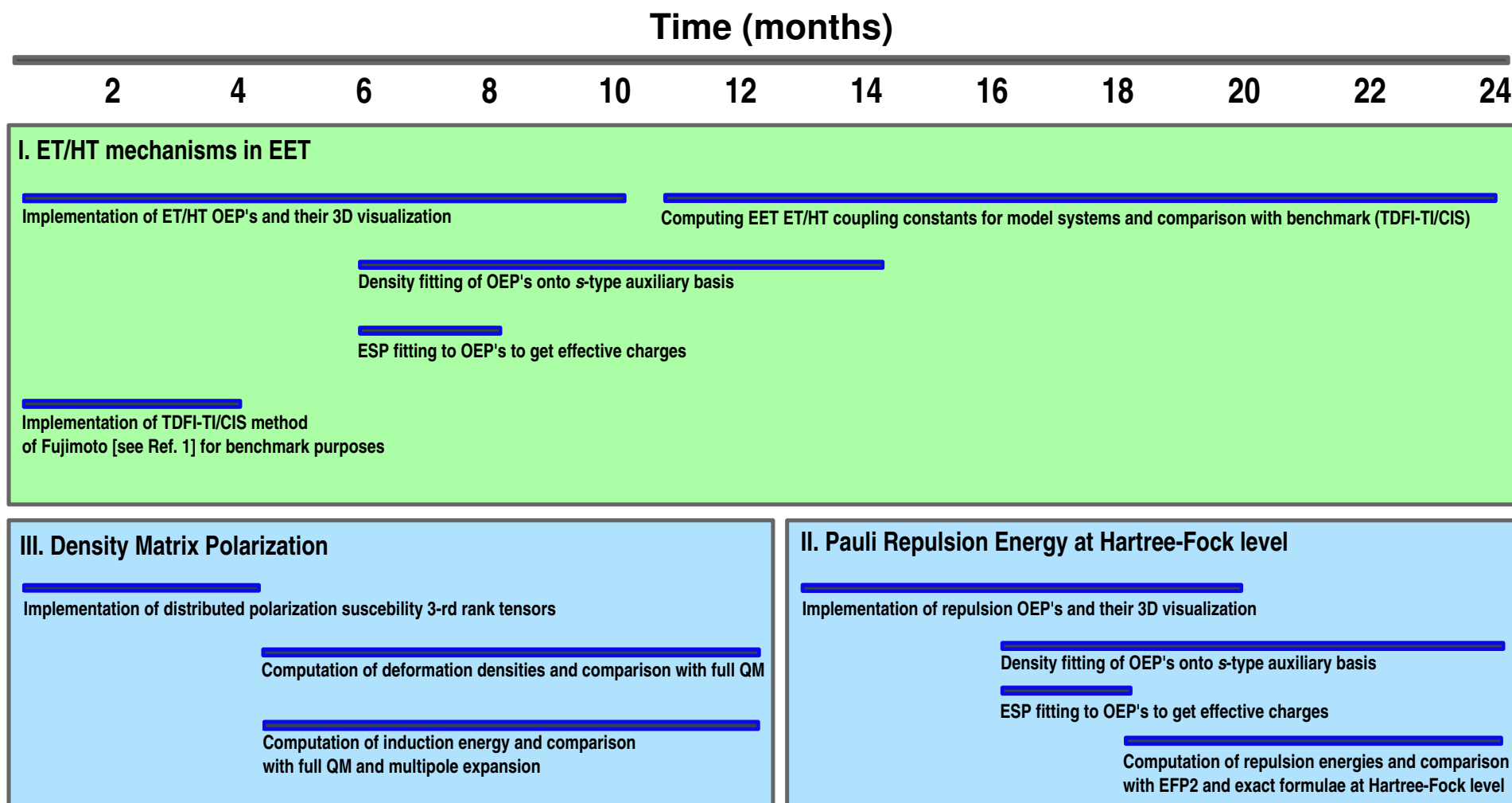


Figure 1: Planned schedule of works. The project coursework is predicted for 4 researchers (3 of them will be full time).

$$f[(\phi_i^A \phi_j^B | \phi_k^B \phi_l^B)] = (\phi_i^A | v_{kl}^B | \phi_j^B) \rightarrow \text{density fitting}, \quad (1b)$$

where A and B denote different molecules and ϕ_i is the i th molecular orbital or basis function. v_{kl}^B is the effective one-electron potential derived from the partial effective densities $\rho_{kl}^B(\mathbf{r}) = \phi_k^B(\mathbf{r})\phi_l^B(\mathbf{r})$. The summations over k and l can be incorporated into the generalized one-electron potential v_{eff}^B to produce

$$\sum_{ij} \sum_{kl \in B} f[(\phi_i \phi_j | \phi_k^B \phi_l^B)] = \sum_{ij} (\phi_i | v_{\text{eff}}^B | \phi_j) . \quad (2)$$

Thus, the total computational effort is extremely reduced from the fourth-fold sum involving evaluation of ERI's to the two-fold sums of cheaper one-electron integrals. It is also possible to generalize the above expression even further by summing over all possible functions f_t

$$\sum_t \sum_{ij} \sum_{kl \in B} f_t[(\phi_i \phi_j | \phi_k^B \phi_l^B)] = \sum_{ij} (\phi_i | v_{\text{eff}}^B | \phi_j) . \quad (3)$$

The above design has the advantage that the effective potentials are fully first-principles and no extensive case-dependent fitting procedures are necessary. Only the effective potentials of *independent* fragment B need to be determined once and for all. **Note also that, in principle, there is no approximation made here at that moment.** Thus, many quantities P could be generally expressed as

$$P = \sum_{ij} \sum_p \mathcal{F}_p[(i | \hat{v}_{\text{eff}}^p(1) | j)] , \quad (4)$$

where $\hat{v}_{\text{eff}}^p(1)$ is a one-electron operator, \mathcal{F} is the functional representing the environment and i, j refer to atomic or molecular orbitals.

4.2 Effective One-Electron Potentials: Examples

Some illustrative examples of using the above rules are provided next. Owing to appropriate recasting of complicated equations involving summations over ERI's, the proposed technique could find applications in quite a few unrelated fundamental areas of theoretical chemistry. Note however that the explicit mathematical forms of the effective potentials are not shown in this Proposal since they can be worked out by applying the rules presented in Section 4.1.

4.2.1 EET Coupling Constants

OEP technique of simplifying equations can be fruitfully applied to the evaluation of specific quantities such as excitation energy transfer couplings between electronic vertical transitions of coupled chromophores.⁶


In the simplest case the EET coupling constant can be written as

$$V_{AB} = J_{AB} + K_{AB} . \quad (5)$$

It was shown before that the Coulombic coupling J_{AB} can be computed analytically with good accuracy by using *ab initio* distributed transition multipoles.²³ The exchange part K_{AB} is relatively small in many cases. Eq. (5) can however be not sufficient when electron/hole transfer (ET/HT) mechanisms are important which is the case when the electronic chromophores are close to each other.⁵

To illustrate the concept, electron transfer (ET) contribution⁵ is considered below (Figure 2). By utilizing the OEP technique, one can achieve a significant simplification of the original expressions derived by Fujimoto⁵ under the assumption that the density matrix is diagonal in AO representation

$$V_{\text{ET1}} \cong t_{H \rightarrow L}^A \left[\left(\phi_L^A | \hat{F} | \phi_L^B \right) + 2 \left(\phi_L^A \phi_H^A | \phi_H^A \phi_L^B \right) - \left(\phi_L^A \phi_L^B | \phi_H^A \phi_H^A \right) \right]$$

 **Define OEP's**

$$V_{\text{ET1}} \cong t_{H \rightarrow L}^A \left\{ \left(\phi_L^A | -\frac{1}{2} \nabla^2 | \phi_L^B \right) + \sum_{\mu \in A} \sum_{\sigma \in B} \left[\left(\mu | v_{\text{ET1}}^{A[\mu]} | \sigma \right) C_{\sigma L}^B + (C_{\mu L}^A)^* \left(\mu | v_{\text{ET1}}^{B[\sigma]} | \sigma \right) \right] \right\}$$

Figure 2: Defining OEP's drastically simplifies the expression for the contribution of ET to EET coupling constant. In this Figure, $t_{H \rightarrow L}$ denotes the CI coefficient of the HOMO-LUMO excitation. Greek subscripts denote atomic basis functions, $\phi_{H(L)}$ denotes molecular HOMO (LUMO) orbital whereas $C_{\mu L}$ is the associated wave function LCAO-MO coefficient. Complicated calculations of ERI's are replaced by much cheaper evaluation of one-electron integrals.

and has non-zero blocks only for chromophores A and B . Similar manipulations can be continued for V_{ET2} , as well as V_{HT1} , V_{HT2} , V_{CT1} and V_{CT2} derived in original paper.⁵ Thus, once the appropriate OEP's for short range electron and hole transfer process are implemented and tested, estimation of the associated coupling constants would become much cheaper computationally.

Model Systems and Applications. The proposed method will be tested on small model systems such as dimers of ethylene or naphthalene, as well as chlorophyll subunits within the light-harvesting complexes and reaction centres. The results will be tested against more accurate schemes such as transition density fragment interaction with transfer integral correction (TDFI-TI) method.⁵ The above presented OEP-based formulation could efficiently and accurately describe Dexter electron transfer mechanism that occurs at short interchromophore distances and is important for deeper understanding the energy transfer in photosynthesis as well as in systems build of artificial antenna complexes.

4.2.2 Repulsive Interactions

Similar reductions in the complexity of equations can be achieved for Pauli repulsion originating from the wave function overlap between the interacting species. As an example, theoretical model of Murrell et al.²⁴ is considered here (Figure 3) since the first-order term was a starting point for developing the Pauli repulsion potential²⁵ for the EFP2 method¹⁹ that is nowadays widely used and developed by the scientific community.^{2,22} By using the concept of OEP's one can re-write the original expressions of Murrell et al.'s and the fully equivalent form is composed solely of the calculations of overlap integrals between occupied molecular orbitals of one molecule and specifically adjusted auxiliary basis set functions centered on the other molecule. The coefficients of the auxiliary basis set can be computed analytically from the generalized density fitting scheme[†]

$$\mathbf{G}_i = \mathbf{s}^{-1} \mathbf{v}_i, \quad (6)$$

where $s_{\xi\xi'} = (\xi | \xi')$ and the ξ th component of vector \mathbf{v}_i is given by

$$v_{\xi i} \equiv (i | v_{\text{eff},1}^A | \xi) - \sum_{k \in A} \left(k | v_{\text{eff},2}^{A;k} | \xi \right) + (i | v_{\text{nuc}}^A | \xi) \quad (7)$$

with the one-electron potentials $v_{\text{eff},1}^A$, $v_{\text{eff},2}^{A;k}$ and v_{nuc}^A being fully first-principles and characteristic to molecule A only (and the same is defined for molecule B). Thus, the effective potential associated with the i th occupied MO is defined here as $v_{\text{eff}}^{A;i}(\mathbf{r}) \equiv \sum_{\xi} G_{\xi i} \xi(\mathbf{r})$.

[†] See Ref.[26] for the density fitting.

$$\begin{aligned}
U_{\text{rep}}(\mathcal{O}(S)) = -2 \sum_{i \in A} \sum_{j \in B} S_{ij} & \left\{ V_{ij}^A + V_{ij}^B + \sum_{k \in A} \left(2 \left(\phi_i^A \phi_j^B | \phi_k^A \phi_k^A \right) - \left(\phi_i^A \phi_k^A | \phi_k^A \phi_j^B \right) \right) \right. \\
& \left. + \sum_{l \in B} \left(2 \left(\phi_i^A \phi_j^B | \phi_l^B \phi_l^B \right) - \left(\phi_i^A \phi_l^B | \phi_l^B \phi_j^B \right) \right) \right\} \\
& \Downarrow \text{Define OEP's} \\
U_{\text{rep}}(\mathcal{O}(S)) = -2 \sum_{i \in A} \sum_{j \in B} S_{ij} & \left\{ \sum_{\xi \in A} (\xi | j) G_{\xi i}^A + \sum_{\zeta \in B} (\zeta | i) G_{\zeta j}^B \right\}
\end{aligned}$$

Figure 3: Defining OEP's within the Murrell et al.'s expression²⁴ for the first order contribution to the Pauli repulsion energy at Hartree–Fock level drastically simplifies the original equation. In this Figure, i and j denote occupied molecular orbitals, S_{ij} is the corresponding overlap integral, V_{ij}^X is the matrix element of the electron-nucleus attraction operator for nuclei in molecule X . Formulation of OEP's requires the auxiliary basis set (ξ and ζ) with expansion coefficients $G_{\xi i}$ and $G_{\zeta j}$, that are determined once and for all for isolated molecules according to Eq. (6).

Similar OEP trick can be done for the approximate contribution due to square of overlap matrix element, derived by Jensen and Gordon.²⁵ The new result involving OEP's reads

$$U_{\text{rep}}(\mathcal{O}(S^2)) \cong 2 \sum_{i \in A} \sum_{j \in B} S_{ij}^2 \left\{ \left(i | v_{\text{eff},3}^{B;j} | i \right) + \left(j | v_{\text{eff},3}^{A;i} | j \right) \right\}, \quad (8)$$

which is a significant simplification over the original equation (see Eq. (38) in Ref. [25]). It is emphasized that the formulae shown above are *not* approximations but are fully equivalent to their original counterparts.

Model Systems and Applications. The OEP-based model of Pauli repulsion energy shall be tested on small dimeric complexes at Hartree–Fock level of theory. Since the original results of Murrell et al.²⁴ and Jensen and Gordon²⁷ quoted here have been used to construct the Pauli repulsion potential in the EFP2 method, OEP-based analogue will be compared with EFP2 in terms of accuracy and speed. It is anticipated that, while EFP2 Pauli repulsion model contains further approximations, OEP-based formulation is less approximate and is believed to be at least as efficient as EFP2-based calculation.

4.2.3 Electric Field-Induced Polarization of Density Matrix

The simple first-principles model for prediction of the polarization-induced electron density change of structurally unrelaxed molecule is proposed here. The associated change in the density matrix, $\delta \mathbf{D}$, is deconvoluted into a product form of the polarization susceptibility \mathbf{B} and induced dipole moments $\delta \boldsymbol{\mu}_i$ due to electric fields \mathbf{E}_i at the centroids of the occupied molecular orbitals,

$$\delta \mathbf{D} \approx \sum_i^{\text{occ}} [\text{polarization susceptibility of the } i\text{th MO}] \cdot \delta \boldsymbol{\mu}_i \rightarrow \sum_i^{\text{occ}} \mathbf{B}_{\mu\nu}^{(i)} \cdot \mathbf{E}_i. \quad (9)$$

While $\delta \boldsymbol{\mu}_i$ contain critical information about the polarization of the electronic cloud, polarization susceptibility is a property of unperturbed molecule and can be precomputed once and for all. This could be adapted into an efficient effective one-electron fragment potential.

For this Project, approximate analytic expressions of the polarization susceptibility tensors at the Hartree–Fock level were worked out by analysing the changes in the LCAO-MO coefficients upon

the induction process under the condition of idempotence restraint of the one-particle density matrix. Application of the proposed method requires calculation of the induced dipole moments associated with the molecular orbitals which were modelled by the distributed polarizabilities. The preliminary results are shown for water molecule in Figure 4 where constant electric field was applied in several directions. The newly developed model shown here for the first time works qualitatively well for

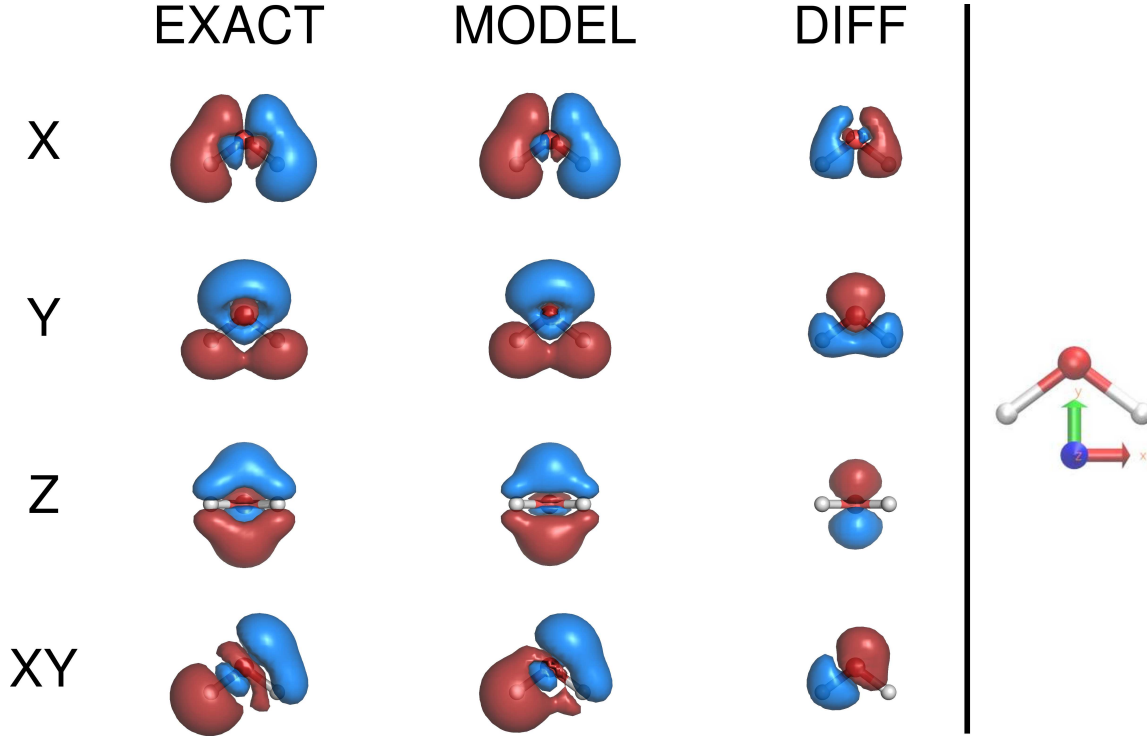


Figure 4: First version of the here proposed first-principles density matrix polarization susceptibility tensor model works qualitatively well in describing the electron polarization in uniform electric field. Polarization deformation densities of water (H_2O) due to external uniform electric fields, were obtained by using HF/6-311++G** method ('EXACT') and the proposed model ('MODEL'; Eq. (9)) derived at the same level. In this Figure, the difference $\Delta\rho^{\text{DIFF}} \equiv \Delta\rho^{\text{EXACT}} - \Delta\rho^{\text{MODEL}}$, which is denoted as 'DIFF', is also plotted. The following electric field directions were tested (x, y, z , in au): 'X': (0.015, 0, 0); 'Y': (0, 0.015, 0); 'Z': (0, 0, 0.015); 'XY': (0.010607, 0.010607, 0). The isocontours were plotted for ± 0.001 au. Orientation of a water molecule is shown in the inset at the right hand side of the Figure.

water molecule but it should be improved to reach chemical accuracy. Once the good model of the density polarization is further developed and tested, it can be combined with the effective potential approach and polarization energy could be efficiently computed. It is worth mentioning that, at that moment, there is no simple *ab initio* method of computation of electron deformation densities without considering the entire molecular aggregate.^{28,29} Therefore, it is believed that the proposed model is a good candidate for an accurate and efficient method for prediction of electronic density polarization.

One of the advantages of using the density polarization method is that the exchange-overlap and exchange-induction effects could be inherently built in the model of interaction energy or molecular dynamics. In particular, one needs to resolve the problem of computing the following class of integrals¹⁸ $\iint \frac{\rho^X(\mathbf{r}_1)\Delta\rho^{\text{Pol}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$, where $\rho^X(\mathbf{r}_1)$ is a known one-electron density (e.g., Pauli deformation density¹⁸) and $\Delta\rho^{\text{Pol}}$ is the polarization deformation density. Therefore, using the deformation susceptibility tensor from Eq. (9) the above integral can be greatly simplified as follows

$$\iint \frac{\rho^X(\mathbf{r}_1)\Delta\rho^{\text{Pol}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \equiv \sum_{\alpha\beta} D_{\alpha\beta}^X \sum_{i \in A}^{\text{occ}} \left(\alpha | \mathbf{v}_{\text{Pol}}^{(i)} | \beta \right) \cdot \mathbf{E}_i, \quad (10)$$

where the new effective one-electron potential is defined without loss of generality as

$$\mathbf{v}_{\text{Pol}}^{(i)}(\mathbf{r}) \equiv \sum_{\mu\nu \in A} \left[\int \frac{\phi_\mu(\mathbf{r}')\phi_\nu(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \mathbf{B}_{\mu\nu}^{(i)}. \quad (11)$$

Model Systems and Applications. The proposed model of density polarization will be tested on small molecules under external (uniform and non-uniform) electric fields, as well as molecular aggregates. It is believed that it will be a fundamental of more general method for efficient computation of the interaction energies by using electron density-based scheme that can be essentially free from multipole expansion.

4.3 Range of Applications of Effective One-Electron Potentials

While defining smart one-electron effective potentials might drastically simplify equations and their evaluations for larger molecular systems, there are situations in which there is no way to simplify summations over ERI's by using technique described in previous sections. One of the obstacles is tackling integrals of the form $(\phi^A \phi^B | \phi^A \phi^B)$. Example of use of such difficult integrals is evaluation of the exchange energy which is an attractive part of exchange-repulsion potential. Satisfactory solution of this problem is using the spherical Gaussian overlap approximation by Jensen³⁰ which was shown by him to provide accurate estimations of the exchange energy at the SCF level. However, neither this trick nor the OEP technique can be applied for fast evaluation of exchange contribution to EET coupling constant, K_{AB} (cf. Eq. (5)). It is however not so surprising – there are processes which have significantly two-electron character, thus preventing from using one-electron potentials. Nevertheless, there is some evidence that these two-electron effects are rather rarely of significant strengths and virtually one-electron effects, even if blurred by appearance of complicated two-electron integrals, can be extracted and used extensively in basically all fields of quantum chemistry of large, extended molecular aggregates.

This project focuses on fundamentals of using OEP's and therefore will consider only Hartree–Fock and configuration interaction with singles (CIS) for the description of ground and electronic excited states, respectively. However, it is anticipated here that once low-level theories are developed and tested, one could further attempt to formulate more accurate schemes that will take into account electron correlation rigorously.

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