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Soumi Haldar, Achintya Kumar Dutta

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A Multi-layer Approach to the Equation of Motion Coupled-Cluster Method for the Electron affinity

Soumi Haldar and Achintya Kumar Dutta*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076

We have presented a multi-layer implementation of the equation of motion coupled-cluster method for the electron affinity, based on local and pair natural orbitals. The method gives consistent accuracy for both localized and delocalized anionic states. It results in many fold speed-up in computational timing as compared to the canonical and DLPNO based implementation of the EA-EOM-CCSD method. We have also developed an explicit fragment-based approach which can lead to even higher speed-up with little loss in accuracy. The multi-layer method can be used to treat the environmental effect of both bonded and non-bonded nature on the electron attachment process in large molecules.

*achintya@chem.iitb.ac.in

1. Introduction:

Electron attachment plays an essential role in many of the biological processes, which include photosynthesis, respiration, and radiation damage to biomolecules. Theoretical simulations can play a significant role in understanding the physics and the chemistry of the electron attachment induced biological processes.

The quantum chemical methods available for the study of electron affinity can be classified into two broad categories. The first one is the so-called Δ -based method, in which one needs to perform two separate calculations on the neutral and the electron attached state. Consequently, the electron affinity is calculated as the difference between the two separately calculated energies. Now, the quantum chemical calculations on the anionic state may suffer from problems like spin contamination and symmetry breaking in the wave-function. Moreover, the reference Hartree-Fock wave-function of the anionic state may suffer from variational collapse. Jordan and co-workers¹ have recently shown that a variational collapse of the reference wave-function cannot be cured by even a CCSD(T) treatment of the correlation effect. On the other hand, the direct difference energy based methods, which calculate the electron affinity directly as the energy of transition from the neutral to the anionic state, is free from the problems mentioned above and can calculate electron affinity corresponding to multiple states in a single calculation. The method based on Green's function², propagator based methods^{3,4}, linear response method⁵, and equation of motion (EOM)⁶, all fall under this category. Among all the direct difference energy based methods, the equation of motion coupled cluster (EOM-CC)⁷⁻¹¹, is considered to be the most accurate and systematically improvable one. The EOM-CC is generally used in singles and doubles approximation (EOM-CCSD), which scales as iterative $O(N^6)$ power of the basis set and has an error bar¹² of 0.01 to 0.03 eV for the electron attachment problem. The steep computational scaling and high storage requirement restrict the use of the canonical EOM-CCSD method beyond small molecules unless one has access to supercomputing facilities. Various strategies have been described in the literature¹³ to reduce the scaling of the EOM-CCSD calculations. Starting from perturbative approximation¹⁴⁻¹⁹, density fitting²⁰⁻²⁶ and semi-numerical approximation²⁷⁻²⁹ to the state of the art implementations³⁰⁻³⁹ based on local orbital and natural orbitals has been reported in the literature. However, the reports of lower scaling approximation to electron attachment variant of the EOM-CCSD method (EA-EOM-CCSD) are rather limited^{40,41}. Recently, Neese and co-workers have developed a domain-based pair natural implementation (DLPNO⁴²⁻⁵⁰) of the EA-EOM-CCSD method⁵¹, which can be applied to large molecules. However, most of the existing implementation of the EA-EOM-CCSD method is restricted to isolated gas-phase molecules only. The surrounding environment can have a significant impact on the electron attachment process as the incoming electron is often

delocalized. Therefore, it is a challenging task to develop theoretical models that can describe environmental effects on the electron attachment process.

The theoretical models that are usually used to describe environmental effects on quantum chemical calculations are of two types: (i) implicit model and (ii) explicit model. The implicit solvation models^{52,53} treat the whole environment as a uniform polarisable continuous medium, with a specific dielectric constant. The polarizable continuum model (PCM)⁵⁴ and conductor-like screening model (COSMO)⁵⁵ are among the most popular implicit models that are used to study the environmental effects introduced by the solvents. However, such implicit models cannot include specific short-range interactions like H-bonding, charge delocalization⁵⁶. The best way to include these short-range interactions is to use an explicit model where each molecule constituting the environment is treated explicitly. However, the explicit treatment of the environment in a quantum chemical method can lead to a high computational cost, even for a medium-sized system. The way-out is to choose a multilayer model in which the entire system is divided into some hypothetical fragments: i) the main system, where the reaction or any chemical change of interest takes place, (ii) the environment, and (iii) the interaction zone between these two fragments. Instead of treating the whole system at a uniform level of theory, different levels of theories can be employed for the different regions depending upon their importance in the chemical process. The multi-layer approach can provide a proper balance between the computational cost and the accuracy of results. Generally, quantum chemical methods (QM) are used to perform the calculation on the main fragments and molecular mechanics (MM) is used for the environment. The treatment of the interaction region varies in different methods. To get a quantitative agreement with the experimental value, one needs to include an accurate treatment of the inter-fragment using the electronic embedding technique.

Additional complications arise when the partitioning between the main system and environment involves cutting of covalent bonds. The most widely used approach is the link atom method⁵⁷, in which the ruptured covalent bonds are saturated with a hydrogen atom. However, this can lead to the introduction of additional degrees of freedom in the system and can also lead to the problem of over-polarization of the QM region by the MM region. Various techniques have been developed to account for the over polarization errors⁵⁸. Alternatively, one can replace the boundary atom by parameterized pseudopotentials^{59,60}. This approach is free from the problem of over polarization. On the downside, the pseudopotentials need to be reparameterized individually on every basis set and for each kind of bond.

The traditional QM/MM methods work reasonably well in describing the environmental effect on the ground state. However, it fails to give a consistent performance for the ionized, electron attached or excited states, especially where the electron density over the environment undergoes significant change

during the transition process⁶¹. Krylov and co-workers have reported some original progress on simulating environmental effects for excited states using a non-empirical polarizable force field in the form of the effective fragment potential method^{62–68}.

The models based on density embedding approaches^{69–71}, on the other hand, are free from the problem mentioned above. It does not require any explicit cutting of bonds and can describe the environmental effects in both ground and excited state. The recent development in the local correlation methods has made it possible to treat the main fragment in a highly accurate wave-function based method and embed it in the density of the environment calculated at a lower-level method (generally Hartree-Fock or the DFT). As there is no semi-empirical parameter involved, the density embedding scheme can be applied to ground and excited states of any arbitrary chemical or biological system. Recent years have seen a surge of interest in the development of coupled cluster based density embedding methods⁷². Manby and co-workers have recently used a projector-based embedding scheme^{73,74} to include environmental effects in EOM-CCSD based excited-state calculations. Kohn and co-workers⁷⁵ have reported a subtractive embedding based approach for the multi-reference coupled-cluster method. Kallay and co-workers^{76,77} have used a Huzinaga equation-based local self-consistent field approach to develop an efficient scheme for the embedding of higher level density functional theory (DFT) and wave function theory (WFT) methods into lower-level DFT or WFT approaches. The multi-layer DLPNO scheme⁷⁸ of Neese and co-workers provides an alternative approach of treating environmental effects in the coupled-cluster based method. In this approach, the localized orbitals are used to distinguish between the central fragment and the environment. Such a localized description of the orbitals allows one to treat different fragments with different levels of accuracy. Straatsma and co-workers⁷⁹ have implemented the multi-layer approach of Divide-Expand-Consolidate (DEC) coupled-cluster method. Folkestad and Koch have also described a multi-layer implementation of excited state coupled-cluster methods based on the correlated natural transition orbitals^{36,80}. Recently, we have extended the multi-layer DLPNO scheme to ionized states⁸¹. The method can describe the environmental effect, of both bonded and non-bonded nature, on the ionization process with systematically controllable accuracy. However, the single ionization is generally localized on a particular part of the molecule and Koopmans' approximation generally provides a decent estimate of the ionization energy for the valence state. However, the situation is entirely different for the electron attachment, as many of the electron attached states can be non-local and the incoming electron can be delocalized on the entire molecule. Moreover, the Hartree-Fock method gives an inadequate description of electron attached states and inclusion of electron correlation is essential to get even a qualitative accuracy in EA value. Therefore, the use of any localized orbital based multi-layer modeling approach to describe the environmental effect on electron attachment can be rather complicated. To the best of our knowledge

no density embedding or multi-layer approach for the direct calculation of electron affinity is available in the literature.

This paper aims to develop a multi-layer DLPNO scheme for electron affinity variant of EOM-CCSD, which can treat the environment effects on the electron attachment to molecules of unprecedented size with systematically controllable accuracy.

2. Theoretical Background:

2.1. Canonical EA-EOM-CCSD:

In the canonical EA-EOM-CCSD method the target electron-attached state is obtained by the diagonalization of the coupled cluster (CC) similarity transformed Hamiltonian

$$\bar{H} = e^{-\hat{T}} H_N e^{\hat{T}} \quad (1)$$

in a space spanned by 1-particle and 2-particle1-hole determinants. The cluster operator $\hat{T}$ is formed out of the ground state CC amplitudes

$$T = T_1 + T_2 + \dots + T_N = \sum_n^N T_n \quad (2)$$

with

$$T_m = \frac{1}{(m!)^2} \sum_{\substack{ij\dots \\ ab\dots}} t_{ij\dots}^{ab\dots} a_a^\dagger a_b^\dagger \dots a_j a_i \quad (3)$$

where the indices $i, j, \dots$ refer to the occupied orbitals while the indices $a, b, \dots$ indicate the virtual ones.

The T amplitudes are obtained by the iterative solution of the following non-linear equations

$$\langle \Psi_{ij\dots}^{ab\dots} | \bar{H} | \Psi_0 \rangle = 0 \quad (4)$$

The EOM-CCSD equation for the k^{th} target state is given by

$$\bar{H} \hat{R}_k | \Psi_0 \rangle = E_k \hat{R}_k | \Psi_0 \rangle \quad (5)$$

where $\hat{R}_k$ is the linear excitation operator and E_k is the energy of the k^{th} target state. The energy difference of the ground and k^{th} target state ($\omega_k = E_k - E_0$) can be directly obtained from the commutator form of the equation,

$$[\bar{H}, \hat{R}_k] | \Psi_0 \rangle = \omega_k \hat{R}_k | \Psi_0 \rangle \quad (6)$$

The explicit expression of the $\hat{R}_k$ operator for electron attachment in the CCSD approximation is given by,

$$\hat{R}_k^{EA} = \sum_a r_a a^\dagger + \sum_a r_{ab}^i b^\dagger a^\dagger i \quad (7)$$

Equation 6 is solved by the modified Davidson iterative diagonalization method, which involves the contraction of the similarity transformed Hamiltonian with suitably chosen guess vectors to generate the so-called sigma vectors. The explicit expressions for the EA-EOM-CCSD sigma vectors are

$$\sigma_a = \underbrace{\tilde{F}_d^a r_d + \tilde{F}_d^l \tilde{r}_{ad}^l}_F + \underbrace{\tilde{g}_{ed}^{la} \tilde{r}_{de}^l}_{3e} \quad (8)$$

$$\begin{aligned} \sigma_{ab}^j = & \underbrace{\tilde{F}_d^a r_{db}^j + \tilde{F}_d^b r_{ad}^j - \tilde{F}_j^l r_{ab}^l - t_{ab}^{mj} \tilde{F}_d^m r_d}_F + \underbrace{\tau_{ab}^{mn} (g_{de}^{mn} r_{de}^j) + \tilde{K}_{bd}^{jl} r_{ad}^l - \tilde{K}_{bd}^{jl} \rho_{da}^l - \tilde{J}_{da}^{jl} \rho_{db}^l}_{2e} \\ & + \underbrace{\tilde{g}_{ba}^{jd} r_d}_{3e} + \underbrace{K(\rho^j, r^j)_{ab}}_{4e} - \underbrace{\tilde{r}_{fe}^m g_{fe}^{nm} t_{ab}^{nj}}_{3b} \end{aligned} \quad (9)$$

Where $\tilde{r}_{ab}^j = 2r_{ab}^j - r_{ba}^j$ and $\rho_{ab}^j = r_{ab}^j + r_a t_b^j$. The g_{rs}^{pq} are two-electron integrals. $\tilde{F}, \tilde{\tilde{F}}, \tilde{g}, \tilde{K}, \tilde{\tilde{K}}$ and $\tilde{J}$ are standard $\bar{H}$ intermediates. The implementational details of the canonical EOM-CCSD in ORCA can be found in reference²⁸.

2.2. DLPNO Implementation of EA- EOM-CCSD:

The implementation of the EA-EOM-DLPNO-CCSD method is based on the idea of local correlation^{42,45,78,82–89} i.e. dynamic correlation is a short-range effect. In the DLPNO approach, the occupied space is expanded in terms of localized orbitals and the virtual space is expanded in correlation domains using projected atomic orbitals. The correlation domains are further truncated using pair natural orbitals (PNOs)⁹⁰. The steps involved in the EA-EOM-DLPNO-CCSD calculations are as follows.

After the solution of the Hartree-Fock equations, we first localized the occupied molecular orbitals to generate localized molecular orbitals (LMO). Any of the standard localization methods like Pipek-Mezey⁹¹, or Foster-Boys⁹² can be used for that purpose.

After localizing the occupied MOs, a linearly dependent (redundant) set of projected atomic orbitals (PAOs)⁸⁴ is constructed for the virtual space.

$$|\tilde{\mu}\rangle = \sum_{\mu} \tilde{P}_{\mu\tilde{\mu}} |\mu\rangle \quad (10)$$

where the PAO coefficient matrix is given by,

$$\tilde{P} = 1 - C^{occ} C^{occ\dagger} S \quad (11)$$

The S is the overlap matrix of atomic orbitals, and C^{occ} represents the occupied block of LMO coefficient matrix.

The advantage of constructing the virtual space PAOs is that the local nature of the orbitals introduced in the occupied space is still retained. A non-redundant set of PAOs ($\tilde{\mu}'$) can then be formed using standard orthonormalization techniques.

In the next step, all these PAOs are assigned to the orbital domains of the occupied LMOs. The domains are defined by a sparse map $L(i \rightarrow \tilde{\mu}_A)$ which includes all the PAOs whose differential overlap integral (DOI)

$$DOI_{i\tilde{\mu}} = \sqrt{\int |i(r)|^2 |\tilde{\mu}(r)|^2} \quad (12)$$

with a particular occupied LMO i is above some predefined threshold value (TCutDO in ORCA). The subscript A indicates that if the PAO $\tilde{\mu}_A$ is centered on the atom A , then all other PAOs which are also centered on the atom A will be included in the orbital domain of occupied LMO i . The pair domains for ij pair are constructed from the union of orbital domains of LMOs i and j . All the required integrals in the DLPNO method is calculated using the density fitting approximation^{20,22–24,93}. Therefore, one also needs to construct a fitting domain of the auxiliary basis for each occupied orbital and is controlled by the keyword TCutMKN in ORCA.

After the construction of the orbital domains, the pairs which will be treated in the coupled-cluster level are determined by a three-step procedure based on a semi-canonical MP2 estimate of the pair energy. The process is controlled by the keyword *TCutPairs* in ORCA. The semi-canonical first order amplitudes for closed-shell species are defined as

$$t_{\tilde{\mu}'_{ij}\tilde{\nu}'_{ij}}^{ij} = \frac{(i\tilde{\mu}'_{ij} | j\tilde{\nu}'_{ij})}{F_{ii} + F_{jj} - \epsilon_{\tilde{\mu}'_{ij}} - \epsilon_{\tilde{\nu}'_{ij}}} \quad (13)$$

where $\tilde{\mu}'_{ij}$ represents the set of non-redundant and linearly independent PAOs in the pair domain for the pair ij . The F_{ii} are the diagonal elements of the Fock matrix in the LMO basis and $\varepsilon_{\tilde{\nu}'_{ij}}$ are the orbital energies in the redundant PAO basis.

In the first step, an MP2 estimate of the pair energy for every pair with $DOI_{ij} < TCutDO_{ij}$ is calculated using a dipole-dipole approximation of the 2-external exchange integrals. The pairs which have the pair energy less than the threshold $TCutPre$ are discarded from the further calculation and the sum of their energies is saved as the weak pair correction. The default values of $TCutDO_{ij}$ and $TCutPre$ are controlled by the keyword $TCutPair$ and is defined as $TCutDO_{ij}=TCutPair/10$ and $TCutPre=TCutPair/100$. In the second step, the semi-canonical MP2 energy is calculated for the remaining pairs in a much smaller domain defined by $2 \times TCutDO$ and $10 \times TCutMKN$ and pairs which have energy smaller than $TCutPairs/10$ are discarded from the pair list. The pair energies of the dropped pairs are added to the existing weak pair correction. In the third step, semi-canonical MP2 energy is calculated for the surviving pairs using larger domains defined by $TCutDO_{ij}$ and $TCutMKN$. The pairs with pair energy larger than $TCutPairs$ (strong pairs) are passed on for the coupled-cluster treatment. The remaining pairs are discarded and their energy is added to the already existing weak pair corrections. The MP2 energy of the strong pair is also saved to be used as a correction for the PNO truncation.

In the next step, pair densities are constructed as

$$D_{\tilde{\mu}'\tilde{\nu}'}^{ij} = \frac{2}{1 + \delta_{ij}} \left(\tilde{t}_{\tilde{\mu}'\tilde{\nu}'}^{ij} \tilde{t}_{\tilde{\mu}'\tilde{\nu}'}^{ij\dagger} - \tilde{t}_{\tilde{\mu}'\tilde{\nu}'}^{ij\dagger} \tilde{t}_{\tilde{\mu}'\tilde{\nu}'}^{ij} \right) \quad (14)$$

with

$$\tilde{t}_{\tilde{\mu}'\tilde{\nu}'}^{ij} = 2t_{\tilde{\mu}'\tilde{\nu}'}^{ij} - t_{\tilde{\nu}'\tilde{\mu}'}^{ij} \quad (15)$$

The pair density D^{ij} is then diagonalized

$$\sum_{\tilde{\nu}'} D_{\tilde{\mu}'\tilde{\nu}'}^{ij} d_{\tilde{\nu}'\tilde{a}_{ij}}^{ij} = n_{\tilde{a}_{ij}}^{ij} d_{\tilde{\mu}'\tilde{a}_{ij}}^{ij} \quad (16)$$

to obtain the PNO occupation numbers $n_{\tilde{a}_{ij}}^{ij}$ and PNO expansion coefficients $d_{\tilde{\mu}'\tilde{a}_{ij}}^{ij}$. All the PNOs with PNO occupation number $n_{\tilde{a}_{ij}}^{ij} \leq TCutPNO$ are discarded and the remaining ones are canonicalized by diagonalizing the virtual-virtual block of the Fock matrix. The MP2 energy is calculated for the strong pairs in the

truncated PNO basis and the difference of it with the MP2 energy in the non-redundant PAO basis is saved as a correction for the PNO truncation.

The next step is to solve the ground state CCSD equations in the truncated PNO basis. Both the singles and doubles amplitudes are expanded in the PNO basis. However, the singles amplitudes are expanded on a PNO basis corresponding to diagonal pairs (singlesPNO) and a tighter threshold ($0.3 \times \text{TCutPNO}$) is used for the singles. The total DLPNO-CCSD correlation energy is thus the sum of the correlation energies for the strong pairs, correction energies for the weak pairs, and the PNO truncation correction. The accuracy of the DLPNO-CCSD method is essentially controlled by four cutoff parameters TCutPNO, TCutPair, TCutMKN and TCutDO, as all the other truncation parameters are defined in terms of these four parameters. Neese and co-workers⁹⁴ have defined a balanced truncation scheme where a single keyword can control all the four truncation parameters. They are called LOOSEPNO, NORMALPNO and TIGHPNO and gives the progressively more accurate results at the expense of higher computational cost. Werner and co-workers^{83,95–100}, as well as, Hattig and co-workers^{101–108} have reported similar developments in the PNO based coupled cluster methods.

In the DLPNO formulation of EA-EOM-CCSD, the singles block of the similarity transformed Hamiltonian is kept untruncated and doubles block is expanded in terms of the singlesPNOs basis. The steps involved in the EA-EOM-DLPNO-CCSD method are as follows.

After the solution of the ground state DLPNO-CCSD equations, one needs to construct the transformation matrix from doublesPNOs ($S_{a_{ij},a}^{ij}$) and singlesPNOs ($S_{\tilde{a}_i,a}^i$) to the canonical basis. In the next step, the virtual-virtual block of the dressed Fock matrix and is constructed as

$$\tilde{F}_a^d = F_a^d - S_{a,\tilde{a}_{mn}}^{mn} \tau_{\tilde{a}_{mn}\tilde{e}_{mn}}^{mn} \bar{g}_{\tilde{d}_{mn}\tilde{e}_{mn}}^{mn} S_{\tilde{d}_{mn},d}^{mn} + S_{a,\tilde{a}_m}^m \bar{g}_{\tilde{d}_m\tilde{e}_m}^{a_m m} t_{e_m}^m S_{\tilde{d}_m,d}^m - S_{a,\tilde{a}_m}^m t_{a_m}^m F_{d_m}^m S_{\tilde{d}_m,d}^m \quad (17)$$

The dressed 2 external integrals are as follows

$$\begin{aligned} \tilde{K}_{\tilde{a}_i\tilde{d}_{il}}^{il} &= K_{\tilde{a}_i\tilde{d}_{il}}^{il} + S_{\tilde{a}_i\tilde{a}_{il}}^{il,il} t_{\tilde{e}_i}^i S_{\tilde{e}_i\tilde{e}_{il}}^{i,il} K_{\tilde{a}_{il}\tilde{d}_{il}}^{\tilde{e}_{il},l} S_{\tilde{d}_{il}\tilde{d}_{il}}^{ll,il} + S_{\tilde{a}_i\tilde{a}_m}^{il,m} t_{\tilde{a}_m}^m (K_{m\tilde{d}_{il}}^{il} + t_{\tilde{e}_i}^i S_{\tilde{e}_i\tilde{e}_{ml}}^{i,ml} K_{\tilde{e}_{ml}\tilde{d}_{ml}}^{ml} S_{\tilde{d}_{ml}\tilde{d}_{il}}^{ml,il}) \\ &+ S_{\tilde{a}_i\tilde{a}_{im}}^{il,im} \tilde{t}_{\tilde{a}_{im}\tilde{e}_{im}}^{im} S_{\tilde{e}_{im}\tilde{e}_{ml}}^{im,ml} K_{\tilde{e}_{ml}\tilde{d}_{ml}}^{ml} S_{\tilde{d}_{ml}\tilde{d}_{il}}^{ml,il} + S_{\tilde{a}_i\tilde{a}_{im}}^{il,im} t_{\tilde{a}_{im}\tilde{e}_{im}}^{im} S_{\tilde{e}_{im}\tilde{e}_{lm}}^{im,lm} K_{\tilde{e}_{lm}\tilde{d}_{lm}}^{lm} S_{\tilde{d}_{lm}\tilde{d}_{il}}^{lm,il} \end{aligned} \quad (18)$$

$$\begin{aligned} J_{\tilde{d}_{il}\tilde{a}_{il}}^{il} &= J_{\tilde{d}_{il}\tilde{a}_{il}}^{il} + S_{\tilde{d}_{il}\tilde{d}_{il}}^{il,il} t_{\tilde{e}_i}^i S_{\tilde{e}_i\tilde{e}_{il}}^{i,il} K_{\tilde{e}_{il}\tilde{a}_{il}}^{l\tilde{d}_{il}} S_{\tilde{a}_{il}\tilde{a}_{il}}^{ll,il} - S_{\tilde{d}_{il}\tilde{a}_m}^{il,m} t_{\tilde{a}_m}^m (J_{m\tilde{d}_{il}}^{il} + t_{\tilde{e}_i}^i S_{\tilde{e}_i\tilde{e}_{ml}}^{i,lm} K_{\tilde{e}_{lm}\tilde{d}_{lm}}^{lm} S_{\tilde{d}_{lm}\tilde{d}_{il}}^{lm,il}) \\ &- S_{\tilde{d}_{il}\tilde{a}_{im}}^{il,im} \tilde{t}_{\tilde{e}_{im}\tilde{a}_{im}}^{im} S_{\tilde{e}_{im}\tilde{e}_{lm}}^{im,lm} K_{\tilde{e}_{lm}\tilde{d}_{lm}}^{lm} S_{\tilde{d}_{lm}\tilde{d}_{il}}^{lm,il} \end{aligned} \quad (19)$$

$$\tilde{\tilde{K}}_{a_{ij}d_{il}}^{il} = 2\tilde{K}_{\tilde{a}_i\tilde{d}_{il}}^{il} - \tilde{J}_{\tilde{d}_{il}\tilde{a}_{il}}^{il} \quad (20)$$

The EA-EOM-DLPNO-CCSD equations are solved using the modified Davidson iterative diagonalization algorithm. The EA-EOM-DLPNO-CCSD sigma equations are as follows

$$\sigma_a = \underbrace{\tilde{F}_d^a r_d + \tilde{F}_{\tilde{a}_l}^a \tilde{r}_{\tilde{a}_l}^l S_{\tilde{a}_l, a}^l}_{F} + \underbrace{g_{\tilde{e}_l, \tilde{d}_l}^{la_l} \tilde{r}_{\tilde{e}_l}^l S_{\tilde{a}_l, a}^l - S_{a, \tilde{a}_m}^m t_{\tilde{a}_m}^{im, l} g_{\tilde{e}_m, \tilde{d}_m}^{im} S_{\tilde{a}_m, \tilde{d}_l}^{im, l} \tilde{r}_{\tilde{e}_l}^l}_{3e} \quad (21)$$

$$\begin{aligned} \sigma_{\tilde{a}_j \tilde{b}_j}^j = & \underbrace{S_{\tilde{a}_j, a}^j \tilde{F}_d^a S_{d, \tilde{a}_j}^j r_{\tilde{d}_j \tilde{b}_j}^j + S_{\tilde{b}_j, b}^j \tilde{F}_d^b S_{d, \tilde{a}_j}^j r_{\tilde{d}_j \tilde{b}_j}^j - \tilde{F}_j^l S_{\tilde{a}_j, \tilde{a}_l}^{j, l} r_{\tilde{a}_l \tilde{b}_l}^l S_{\tilde{b}_l, \tilde{b}_j}^{l, j} - S_{\tilde{a}_j, \tilde{a}_m}^{j, mj} t_{\tilde{a}_m \tilde{b}_m}^{mj} S_{\tilde{b}_m, \tilde{b}_j}^{mj, j} \tilde{F}_d^m S_{\tilde{a}_m, d}^m r_d}_{F} \\ & + \underbrace{S_{\tilde{a}_j, \tilde{a}_{mn}}^{j, mn} \tau_{\tilde{a}_{mn} \tilde{b}_{mn}}^{mn} S_{\tilde{b}_{mn}, \tilde{b}_j}^{mn, j} \left(g_{\tilde{d}_{mn}, \tilde{e}_{mn}}^{mn} S_{\tilde{d}_{mn}, \tilde{d}_j}^{mn, j} r_{\tilde{d}_j \tilde{e}_j}^j S_{\tilde{e}_j, \tilde{e}_{mn}}^{j, mn} \right)}_{2e} \\ & \underbrace{S_{\tilde{b}_j, \tilde{b}_{jl}}^{j, jl} \tilde{K}_{\tilde{b}_{jl} \tilde{d}_{jl}}^{jl} S_{\tilde{d}_{jl}, \tilde{d}_l}^{jl, l} r_{\tilde{a}_l \tilde{d}_l}^l S_{\tilde{a}_l, \tilde{a}_j}^{l, j} - S_{\tilde{b}_j, \tilde{b}_{jl}}^{j, jl} \tilde{K}_{\tilde{b}_{jl} \tilde{d}_{jl}}^{jl} S_{\tilde{d}_{jl}, \tilde{d}_l}^{jl, l} \rho_{\tilde{d}_l \tilde{a}_l}^l S_{\tilde{a}_l, \tilde{a}_j}^{l, j} - S_{\tilde{a}_j, \tilde{a}_{jl}}^{j, jl} \tilde{J}_{\tilde{d}_{jl} \tilde{a}_{jl}}^{jl} S_{\tilde{d}_{jl}, \tilde{d}_l}^{jl, l} \rho_{\tilde{d}_l \tilde{b}_l}^l S_{\tilde{b}_l, \tilde{b}_j}^{l, j}}_{2e} \\ & + \underbrace{g_{\tilde{b}_j \tilde{a}_j}^{j \tilde{d}_j} S_{\tilde{d}_j, d}^j r_d + S_{\tilde{a}_j, \tilde{a}_{jm}}^{j, jm} \tilde{t}_{\tilde{a}_{jm} \tilde{e}_{jm}}^{jm} S_{\tilde{e}_{jm}, \tilde{e}_m}^{jm, m} K_{\tilde{e}_m \tilde{b}_m}^{m \tilde{d}_m} S_{\tilde{a}_m, d}^m r_d S_{\tilde{b}_m, \tilde{b}_j}^{m, j}}_{3e} \\ & - \underbrace{S_{\tilde{a}_j, \tilde{a}_{jm}}^{j, jm} \tilde{t}_{\tilde{a}_{jm} \tilde{e}_{jm}}^{jm} S_{\tilde{e}_{jm}, \tilde{e}_m}^{jm, m} J_{\tilde{b}_m \tilde{e}_m}^{m \tilde{d}_m} S_{\tilde{a}_m, d}^m r_d S_{\tilde{b}_m, \tilde{b}_j}^{m, j} - S_{\tilde{b}_j, \tilde{b}_{jm}}^{j, jm} \tilde{t}_{\tilde{b}_{jm} \tilde{e}_{jm}}^{jm} S_{\tilde{e}_{jm}, \tilde{e}_m}^{jm, m} J_{\tilde{a}_m \tilde{e}_m}^{m \tilde{d}_m} S_{\tilde{a}_m, d}^m r_d S_{\tilde{a}_m, \tilde{a}_j}^{m, j}}_{3e} \\ & + \underbrace{S_{\tilde{a}_j, \tilde{a}_{mn}}^{j, mn} \left(2t_{\tilde{a}_{mn} \tilde{b}_{mn}}^{mn} - \tau_{\tilde{a}_{mn} \tilde{b}_{mn}}^{mn} \right) S_{\tilde{b}_{mn}, \tilde{b}_j}^{mn, j} \left(K_{\tilde{a}_{mn}}^{mn} + t_{\tilde{e}_j}^j S_{\tilde{d}_j, \tilde{a}_{mn}}^{j, mn} K_{\tilde{e}_{mn} \tilde{d}_{mn}}^{mn} \right) S_{\tilde{a}_{mn}, d}^{mn} r_d}_{3e} \\ & + \underbrace{K(\rho^j, \mathbf{r}^j)_{\tilde{a}_j \tilde{b}_j}}_{4e} + \underbrace{S_{\tilde{a}_j, a}^{nm, m} \tilde{r}_{\tilde{a}_m}^m S_{\tilde{a}_m, \tilde{a}_j}^{m, nm} g_{\tilde{e}_{nm}, \tilde{e}_m}^{nm} \tilde{f}_{\tilde{a}_m}^m S_{\tilde{a}_j, \tilde{a}_{nj}}^{j, nj} t_{\tilde{a}_{nj} \tilde{b}_{nj}}^{nj} S_{\tilde{b}_{nj}, \tilde{b}_j}^{nj, j}}_{3b}. \end{aligned} \quad (22)$$

where

$$\tau_{\tilde{a}_j \tilde{b}_j}^{ij} = t_{\tilde{a}_j \tilde{b}_j}^{ij} + t_{\tilde{a}_j}^i t_{\tilde{b}_j}^j \quad (23)$$

$$\tilde{t}_{\tilde{a}_j \tilde{b}_j}^{ij} = 2t_{\tilde{a}_j \tilde{b}_j}^{ij} - t_{\tilde{b}_j \tilde{a}_j}^{ij} \quad (24)$$

$$\tilde{r}_{\tilde{a}_j \tilde{b}_j}^j = 2r_{\tilde{a}_j \tilde{b}_j}^j - r_{\tilde{b}_j \tilde{a}_j}^j \quad (25)$$

$$\rho_{\tilde{a}_j \tilde{b}_j}^j = r_{\tilde{a}_j \tilde{b}_j}^j + S_{\tilde{a}_j, a}^j r_a^j t_{\tilde{b}_j}^j. \quad (26)$$

The term containing the four external integrals is constructed as

$$\begin{aligned} K(\rho^j, \mathbf{r}^j)_{\tilde{a}_j \tilde{b}_j} = & S_{\tilde{a}_j, \tilde{a}_{jj}}^{j, jj} g_{\tilde{c}_{jj} \tilde{d}_{jj}}^{\tilde{a}_{jj} \tilde{b}_{jj}} S_{\tilde{b}_{jj}, \tilde{b}_j}^{jj, j} S_{\tilde{c}_{jj}, \tilde{c}_j}^{jj, j} \rho_{\tilde{c}_j \tilde{d}_j}^j S_{\tilde{d}_j, \tilde{d}_{jj}}^{j, jj} \\ & - \left(S_{\tilde{a}_j, \tilde{a}_m}^{j, m} t_{\tilde{a}_m}^m g_{\tilde{c}_{mm} \tilde{d}_{mm}}^{m \tilde{b}_{mm}} S_{\tilde{b}_{mm}, \tilde{b}_j}^{mm, j} - S_{\tilde{b}_j, \tilde{b}_m}^{j, m} t_{\tilde{b}_m}^m g_{\tilde{c}_{mm} \tilde{d}_{mm}}^{\tilde{a}_{mm} m} S_{\tilde{a}_{mm}, \tilde{a}_j}^{mm, j} \right) S_{\tilde{c}_{mm}, \tilde{c}_j}^{mm, j} r_{\tilde{c}_j \tilde{d}_j}^j S_{\tilde{d}_j, \tilde{d}_{mm}}^{j, mm} \end{aligned} \quad (27)$$

For more details on the implementation of EA-EOM-DLPNO-CCSD, authors can consult reference 51.

From equations 21 and 22, one can see that the different terms in EA-EOM-DLPNO-CCSD method are treated with different levels of accuracy. The singles contribution to singles block, which has the zeroth-order contribution to the electron affinity, is kept untruncated. The singles contribution to doubles, doubles contribution to singles and doubles contribution to doubles block, whose contributions are at least up to second-order in perturbation, are treated in terms of singlesPNOs basis. The terms which are higher than the second-order are calculated in terms of doublesPNOs basis and transformed back to the singlesPNOs basis on the fly. In addition to the four standard truncation parameters for DLPNO-CCSD method, the singlesPNOs truncation parameter (TCutPNOSingles in ORCA) plays a crucial role in determining the accuracy of the calculated electron affinity. We have used a default value of 10^{-12} for the TCutPNOSingles in this paper, which is slightly larger than that used in the original EA-EOM-DLPNO-CCSD implementation paper⁵¹.

2.3. Multi-layer EA-EOM-DLPNO-CCSD:

The multi-layer DLPNO method uses localized orbitals to partition the system into multiple hypothetical fragments and the fragmentation scheme is based on the chemical intuition of the users. The incoming electron must be localized in one of the fragments (main fragment denoted by 1 in Figure 1) for the applicability of the multi-layer EA-EOM-DLPNO-CCSD method. The other fragments can be considered as the environment which participates in the electron attachment process. The fragments may or may not be covalently bonded with each other.

In the multi-layer EA-EOM-DLPNO-CCSD method, the Hartree-Fock (HF) calculation is performed on the entire system at first. After the HF step, the occupied orbitals are localized and assigned to a particular fragment based on their Mulliken populations. Next, the orbital domains and PNOs for the different sets of fragments are constructed using different truncation thresholds. The sigma equations for multi-layer EA-EOM-DLPNO-CCSD methods are as follows

$$\sigma_a = \tilde{F}_d^a r_d + \tilde{F}_{\tilde{d}_{l_x}}^{l_x} \tilde{r}_{\tilde{a}_{l_x}}^{l_x} S_{\tilde{a}_{l_x},a}^{l_x} + g_{\tilde{e}_{l_x} \tilde{d}_{l_x}}^{l_{a_{l_x}}} \tilde{r}_{\tilde{e}_{l_x} \tilde{d}_{l_x}}^{l_x} S_{\tilde{a}_{l_x},a}^{l_x} - S_{a,\tilde{a}_{m_x}}^{m_x} t_{\tilde{a}_{m_x}}^{m_x} S_{\tilde{e}_{l_x} \tilde{d}_{l_x m_y}}^{l_x m_y} K_{\tilde{e}_{l_x m_y} \tilde{d}_{l_x m_y}}^{l_x m_y} S_{\tilde{d}_{l_x m_y} \tilde{a}_{l_x}}^{l_x m_y} \tilde{r}_{\tilde{e}_{l_x} \tilde{d}_{l_x}}^{l_x} \quad (28)$$

$$\begin{aligned}
\sigma_{\tilde{a}_j \tilde{b}_j}^j &= S_{\tilde{a}_{jx}, a}^{jx} \tilde{F}_d^a r_d S_{d, \tilde{a}_{jx}}^{jx} r_{\tilde{a}_{jx}, \tilde{b}_{jx}}^{jx} + S_{\tilde{b}_{jx}, b}^{jx} \tilde{F}_d^b S_{d, \tilde{a}_{jx}}^{jx} r_{\tilde{a}_{jx}, \tilde{b}_{jx}}^{jx} + \tilde{F}_d^{l_y} S_{\tilde{a}_{jx}, \tilde{a}_{ly}}^{jx, l_y} r_{a_{ly}, b_{ly}}^{l_y} S_{\tilde{b}_{ly}, \tilde{b}_{jx}}^{l_y, jx} \\
&- S_{\tilde{a}_{jy}, \tilde{a}_{m_y jx}}^{jx, m_y jx} t_{\tilde{a}_{m_y jx}, \tilde{b}_{m_y jx}}^{m_y jx} \tilde{F}_{d_{m_y}}^{m_y} S_{\tilde{d}_{m_y}, d}^{m_y} r_d + S_{\tilde{a}_{jx}, \tilde{a}_{m_y n_z}}^{jx, m_y n_z} \tau_{\tilde{a}_{m_y n_z}, \tilde{b}_{m_y n_z}}^{m_y n_z} S_{\tilde{b}_{m_y n_z}, \tilde{b}_{jx}}^{m_y n_z, jx} (g_{\tilde{a}_{m_y n_z}, \tilde{e}_{m_y n_z}}^{m_y n_z} S_{\tilde{d}_{m_y n_z}, e_{m_y n_z}}^{m_y n_z, jx} r_{\tilde{d}_{jx}, \tilde{e}_{jx}}^{jx} S_{\tilde{e}_{jx}, \tilde{e}_{m_y n_z}}^{jx, m_y n_z}) \\
&+ S_{b_{jx}, b_{jxly}}^{jx, l_y} K_{b_{jxly}, d_{jxly}}^{jxly, l_y} S_{d_{jxly}, d_{ly}}^{jxly, l_y} r_{a_{ly}, d_{ly}}^{l_y} S_{a_{ly}, a_{jx}}^{l_y, jx} - S_{b_{jx}, b_{jxly}}^{jx, l_y} K_{b_{jxly}, d_{jxly}}^{jxly, l_y} S_{d_{jxly}, d_{ly}}^{jxly, l_y} \rho_{d_{ly}, a_{ly}}^{l_y} S_{a_{ly}, a_{jx}}^{l_y, jx} \\
&- S_{a_{jx}, a_{jxly}}^{jx, l_y} J_{d_{jxly}, a_{jxly}}^{jxly, l_y} S_{d_{jxly}, d_{ly}}^{jxly, l_y} \rho_{d_{ly}, b_{ly}}^{l_y} S_{b_{ly}, b_{jx}}^{l_y, jx} + g_{b_{jx}, a_{jx}}^{jx, d_{jx}} S_{d_{jx}, d}^{jx} r_d + S_{a_{jx}, a_{jxm_y}}^{jx, jxm_y} t_{a_{jxm_y}, e_{jxm_y}}^{jxm_y} S_{e_{m_y jx}, e_{m_y}}^{jxm_y, m_y} K_{e_{m_y}, b_{m_y}}^{m_y, d_{m_y}} S_{d_{m_y}, d}^{m_y, jx} r_d S_{b_{m_y}, b_{jx}}^{m_y, jx} \quad (29) \\
&- S_{a_{jx}, a_{jxm_y}}^{jx, jxm_y} t_{a_{jxm_y}, e_{jxm_y}}^{jxm_y} S_{e_{m_y jx}, e_{m_y}}^{jxm_y, m_y} J_{b_{m_y}, e_{m_y}}^{m_y, d_{m_y}} S_{d_{m_y}, d}^{m_y, jx} r_d S_{b_{m_y}, b_{jx}}^{m_y, jx} - S_{b_{jx}, b_{jxm_y}}^{jx, jxm_y} t_{e_{jxm_y}, b_{jxm_y}}^{jxm_y} S_{e_{m_y jx}, e_{m_y}}^{jxm_y, m_y} J_{a_{m_y}, e_{m_y}}^{m_y, d_{m_y}} S_{d_{m_y}, d}^{m_y, jx} r_d S_{a_{m_y}, a_{jx}}^{m_y, jx} \\
&+ S_{a_{jx}, a_{m_y n_z}}^{jx, m_y n_z} (2t_{a_{m_y n_z}, b_{m_y n_z}}^{m_y n_z} - \tau_{a_{m_y n_z}, b_{m_y n_z}}^{m_y n_z}) S_{b_{m_y n_z}, b_{jx}}^{m_y n_z, jx} (K_{id_{m_y n_z}}^{m_y n_z} + t_{e_{jx}}^{jx} S_{e_{jx}, e_{m_y n_z}}^{jx, m_y n_z} K_{e_{m_y n_z}, d_{m_y n_z}}^{m_y n_z}) S_{d_{m_y n_z}, d}^{m_y n_z, jx} r_d + K(\rho^{jx}, r^{jx})_{a_{jx}, b_{jx}} \\
&- S_{e_{n_z m_y}, e_{m_y}}^{n_z m_y, m_y} r_{f_{m_y}, e_{m_y}}^{m_y} S_{f_{m_y}, f_{n_z m_y}}^{m_y, n_z m_y} S_{a_{jx}, a_{n_z jx}}^{n_z jx} t_{a_{n_z jx}, b_{n_z jx}}^{n_z jx} S_{b_{n_z jx}, b_{jx}}^{n_z jx, jx}
\end{aligned}$$

The virtual-virtual block of the dressed Fock matrix in the multi-layer DLPNO formulation is given by,

$$\tilde{F}_a^d = F_a^d - S_{a, \tilde{a}_{m_x n_y}}^{m_x n_y} \tau_{\tilde{a}_{m_x n_y}, \tilde{e}_{m_x n_y}}^{m_x n_y} \bar{g}_{\tilde{a}_{m_x n_y}, \tilde{e}_{m_x n_y}}^{m_x n_y} S_{\tilde{d}_{m_x n_y}, d}^{m_x n_y} + S_{a, \tilde{a}_{m_x}}^{m_x} \bar{g}_{\tilde{a}_{m_x}, \tilde{e}_{m_x}}^{a_{m_x} m_x} t_{e_{m_x}, \tilde{d}_{m_x}}^m S_{\tilde{d}_{m_x}, d}^m - S_{a, \tilde{a}_{m_x}}^{m_x} t_{a_{m_x}, \tilde{d}_{m_x}}^m F_{\tilde{d}_{m_x}}^m S_{\tilde{d}_{m_x}, d}^m \quad (30)$$

The dressed two external integrals are as follows

$$\begin{aligned}
\tilde{K}_{\tilde{a}_{il} \tilde{d}_{il}}^{il} &= K_{\tilde{a}_{ixly}, \tilde{d}_{ixly}}^{ixly} + S_{\tilde{a}_{ixly}, \tilde{a}_{ixly}}^{ixly, l_y} t_{\tilde{e}_{ix}, \tilde{e}_{ixly}}^{ix} S_{\tilde{e}_{ix}, \tilde{e}_{ixly}}^{ix, l_y} K_{\tilde{a}_{ixly}, \tilde{d}_{ixly}}^{\tilde{e}_{ixly}, l_y} S_{\tilde{d}_{ixly}, \tilde{d}_{ixly}}^{l_y, ixly} + S_{\tilde{a}_{ixly}, \tilde{a}_{m_z}}^{ixly, m_z} t_{\tilde{a}_{m_z}}^{m_z} (K_{m_z, \tilde{d}_{ixly}}^{ixly} + t_{\tilde{e}_{ix}}^{ix} S_{\tilde{e}_{ix}, \tilde{e}_{m_zly}}^{ix, m_zly} K_{\tilde{e}_{m_zly}, \tilde{d}_{m_zly}}^{m_zly} S_{\tilde{d}_{m_zly}, \tilde{d}_{ixly}}^{m_zly, ixly}) \\
&+ S_{\tilde{a}_{ixly}, \tilde{a}_{ixm_z}}^{ixly, ixm_z} \tilde{t}_{\tilde{a}_{ixm_z}, \tilde{e}_{ixm_z}}^{ixm_z} S_{\tilde{e}_{ixm_z}, \tilde{e}_{m_zly}}^{ixm_z, l_y} K_{\tilde{e}_{m_zly}, \tilde{d}_{m_zly}}^{m_zly} S_{\tilde{d}_{m_zly}, \tilde{d}_{ixly}}^{m_zly, ixly} + S_{\tilde{a}_{ixly}, \tilde{a}_{ixm_z}}^{ixly, ixm_z} t_{\tilde{a}_{ixm_z}, \tilde{e}_{ixm_z}}^{ixm_z} S_{\tilde{e}_{ixm_z}, \tilde{e}_{ixm_z}}^{ixm_z, l_y} K_{\tilde{e}_{ixm_z}, \tilde{d}_{ixm_z}}^{l_y m_z} S_{\tilde{d}_{ixm_z}, \tilde{d}_{ixly}}^{l_y m_z, ixly}
\end{aligned} \quad (31)$$

$$\begin{aligned}
J_{\tilde{d}_{il} \tilde{a}_{il}}^{il} &= J_{\tilde{d}_{ixly}, \tilde{a}_{ixly}}^{ixly} + S_{\tilde{d}_{ixly}, \tilde{d}_{ixly}}^{ixly, l_y} t_{\tilde{e}_{ix}, \tilde{e}_{ixly}}^{ix} S_{\tilde{e}_{ix}, \tilde{e}_{ixly}}^{ix, l_y} K_{\tilde{e}_{ixly}, \tilde{a}_{ixly}}^{l_y} S_{\tilde{a}_{ixly}, \tilde{a}_{ixly}}^{l_y, ixly} - S_{\tilde{a}_{ixly}, \tilde{a}_{m_z}}^{ixly, m_z} t_{\tilde{a}_{m_z}}^{m_z} (J_{m_z, \tilde{d}_{ixly}}^{ixly} + t_{\tilde{e}_{ix}}^{ix} S_{\tilde{e}_{ix}, \tilde{e}_{lym_z}}^{ix, ly m_z} K_{\tilde{e}_{lym_z}, \tilde{d}_{lym_z}}^{ly m_z} S_{\tilde{d}_{lym_z}, \tilde{d}_{ixly}}^{ly m_z, ixly}) \\
&- S_{\tilde{a}_{ixly}, \tilde{a}_{ixm_z}}^{ixly, ixm_z} \tilde{t}_{\tilde{e}_{ixm_z}, \tilde{a}_{ixm_z}}^{ixm_z} S_{\tilde{e}_{ixm_z}, \tilde{e}_{lym_z}}^{ixm_z, l_y} K_{\tilde{e}_{lym_z}, \tilde{d}_{lym_z}}^{l_y m_z} S_{\tilde{d}_{lym_z}, \tilde{d}_{ixly}}^{l_y m_z, ixly}
\end{aligned} \quad (32)$$

$$\tilde{K}_{a_{il} d_{il}}^{il} = 2\tilde{K}_{\tilde{a}_{ixly}, \tilde{d}_{ixly}}^{ixly} - \tilde{J}_{\tilde{d}_{ixly}, \tilde{a}_{ixly}}^{ixly} \quad (33)$$

The four external term (4e) in the multi-layer DLPNO method is constructed as

$$\begin{aligned}
K(\rho^{jx}, r^{jx})_{\tilde{a}_{jx}, \tilde{b}_{jx}} &= S_{\tilde{a}_{jx}, \tilde{a}_{jx}}^{jx, jx} g_{\tilde{e}_{jx}, \tilde{d}_{jx}}^{\tilde{a}_{jx}, \tilde{b}_{jx}} S_{\tilde{b}_{jx}, \tilde{b}_{jx}}^{jx, jx} S_{\tilde{e}_{jx}, \tilde{c}_{jx}}^{jx, jx} \rho_{\tilde{c}_{jx}, \tilde{d}_{jx}}^{jx} S_{\tilde{d}_{jx}, \tilde{d}_{jx}}^{jx, jx} - (S_{\tilde{a}_{jx}, \tilde{a}_{m_y}}^{jx, m_y} t_{m_y}^{m_y} g_{\tilde{e}_{m_y}, \tilde{d}_{m_y}}^{m_y, m_y} S_{\tilde{b}_{m_y}, \tilde{b}_{jx}}^{m_y, jx} \\
&- S_{\tilde{b}_{jx}, \tilde{b}_{m_y}}^{jx, m_y} t_m^{m_y} g_{\tilde{e}_{m_y}, \tilde{d}_{m_y}}^{m_y, m_y} S_{\tilde{a}_{m_y}, \tilde{a}_{jx}}^{m_y, jx}) S_{\tilde{e}_{m_y}, \tilde{c}_{jx}}^{m_y, jx} r_{\tilde{c}_{jx}, \tilde{d}_{jx}}^{jx} S_{\tilde{d}_{jx}, \tilde{d}_{m_y}}^{jx, m_y}
\end{aligned} \quad (34)$$

The various dressed amplitudes are defined as

$$\begin{aligned}
\tau_{\tilde{a}_{i_x j_y} \tilde{b}_{i_x j_y}}^{i_x j_y} &= t_{\tilde{a}_{i_x j_y} \tilde{b}_{i_x j_y}}^{i_x j_y} + t_{\tilde{a}_{i_x j_y}}^{i_x} t_{\tilde{b}_{i_x j_y}}^{j_y} \\
\tilde{t}_{\tilde{a}_{i_x j_y} \tilde{b}_{i_x j_y}}^{i_x j_y} &= 2t_{\tilde{a}_{i_x j_y} \tilde{b}_{i_x j_y}}^{i_x j_y} - t_{\tilde{b}_{i_x j_y} \tilde{a}_{i_x j_y}}^{i_x j_y} \\
\tilde{r}_{\tilde{a}_{j_x} \tilde{b}_{j_x}}^j &= 2r_{\tilde{a}_{j_x} \tilde{b}_{j_x}}^j - r_{\tilde{b}_{j_x} \tilde{a}_{j_x}}^j \\
\rho_{\tilde{a}_{j_x} \tilde{b}_{j_x}}^j &= r_{\tilde{a}_{j_x} \tilde{b}_{j_x}}^j + S_{\tilde{a}_{j_x}, a}^j r_a^j t_{\tilde{b}_{j_x}}^j
\end{aligned} \tag{35}$$

In all the above cases, if the occupied orbitals x and y both are localized on the main fragment, the terms containing x and y should be treated with the highest possible accuracy (preferably TIGHTPNO or NORMALPNO). If orbital x is localized on the main fragment and the orbital y is localized on the environment, then the term should be treated with the intermediate accuracy. The least accuracy is required when both x and y orbitals are localized on the environment.

Figure 1: A schematic representation of the (a) multi-layer EA-EOM-DLPNO-CCSD method and (b) EF-DLPNO method

The truncation of the singlesPNO basis (TCutPNOSingles) plays a major role in determining the accuracy of the EA-EOM-DLPNO-CCSD method. The value of the TCutPNOSingles for the inter-fragment or environmental interactions is determined from two parameters, the TCutPNO defined for that particular interaction and TCutPNOSingles defined for the main fragment.

$$\text{TCutPNOSingles} = C \times \text{TCutPNO}$$

$$\text{where } C = \frac{\text{TCutPNOSingles}_{\text{main fragment}}}{\text{TCutPNO}_{\text{main fragment}}}$$

One should not completely neglect (treating at the HF level) the intra-fragment interaction from any of the fragments. In the DLPNO implementation of EA-EOM-CCSD method, the doubles block is

truncated using singlesPNO. It ensures that if a particular occupied orbital is localized on the fragment treated at HF level, then all the contributions up to second-order involving that particular orbital get automatically neglected even when one includes the inter-fragment interaction terms for that occupied orbital. The terms containing inter-fragment interaction contributes above second order in perturbation and generally has a small contribution to the total EA. Therefore, one needs to treat the terms up to second order in perturbation at least at LOOSEPNO level to get quantitative accuracy. This leads us to the idea that one can divide the molecule into multiple fragments. The main fragment is treated with NORMALPNO and the rest of the fragments are treated with LOOSEPNO setting. The inter-fragment interactions will be neglected among all the fragments, which will lead to a drastic reduction in the computational cost. The method can give sufficient accuracy as the terms up to second-order are treated at least at LOOSEPNO level even when one neglects all the inter-fragment interactions. We call this new method explicitly fragmented domain based pair natural orbital method (EF-DLPNO) for electron affinity and it is similar in spirit to the cluster in the molecule (CIM) approach of Li and co-workers^{109,110}.

All the EA-EOM-DLPNO-CCSD, DFT and QM/MM calculations are performed using a development version of the software package ORCA¹¹¹. The computational timings are obtained by performing the calculations on two cores of a work station with two hexacore Intel Xeon(R) CPU E5-2643 v4 CPU with 3.40 GHz clock speed and 256 GB total RAM.

3. Results and Discussion:

In this paper, we have mainly focused on the vertical detachment energy (VDE), vertical electron affinity (VEA), and adiabatic electron affinity (AEA). They are defined as follows

$$\text{VDE} = E_{\text{neutral}}(\text{at anion geometry}) - E_{\text{anion}}(\text{at anion geometry})$$

$$\text{VEA} = E_{\text{neutral}}(\text{at neutral geometry}) - E_{\text{anion}}(\text{at neutral geometry})$$

$$\text{AEA} = E_{\text{neutral}}(\text{at neutral geometry}) - E_{\text{anion}}(\text{at anion geometry}).$$

The energy of the k^{th} anionic state is defined as

$$E_{\text{anion}} = E_{\text{HF}} + E_{\text{Corr}} - EA_k$$

where E_{HF} is the HF energy for the neutral species, E_{Corr} is DLPNO strong pair correlation energy for the neutral species and EA_k is the EOMCC electron affinity for that particular state. The energy of the neutral state is defined as

$$E_{\text{neutral}} = E_{\text{HF}} + E_{\text{Corr}}$$

The AEA is determined by separately calculating the energies of the neutral and anion and taking the energy difference. The VDE and VEA values can be directly obtained from the EOM-CCSD output file. The ZPE corrections are not included in any of the EA values.

All the molecules treated in the multi-layer EA-EOM-DLPNO-CCSD method are divided into two fragments: the main fragment and the environment. The various interactions between the two fragments are denoted in the following order: main fragment interaction- inter-fragment interaction- environmental interaction. For example, TPNO-NPNO-LPNO denotes that the main fragment interactions are treated at TIGHTPNO level, the inter-fragment interactions are treated at NORMALPNO level and environmental interactions are treated at LOOSEPNO level.

3.1. Vertical Detachment Energy:

3.1.1. Microsolvated Uracil:

To check the accuracy and efficiency of the multilayer EA-EOM-DLPNO-CCSD method we have chosen a monohydrated uracil system as a simple test case. The initially optimized anion-geometry has been taken from ref ¹¹². The multilayer EA-EOM-DLPNO-CCSD method is an approximation to the standard EA-EOM-DLPNO-CCSD method. Therefore, results from the standard EA-EOM-DLPNO-CCSD calculation on the entire system can be used as the benchmark values for the multilayer EA-EOM-DLPNO-CCSD. This single layer EA-EOM-DLPNO-CCSD calculation on the whole system has been performed using the TIGHTPNO settings.

Figure 2: The natural orbitals corresponding to the (a) valence bound and (b) dipole bound state of monohydrated uracil anion

In this paper, we have focused only on the bound anionic states and we found the existence of two bound states for monohydrated uracil. In the first state, the additional electron density is found to be localized on the nuclear framework of uracil. The extra electron in the second state is away from the nuclear framework and is bound by charge dipole interaction (Figure 2). They are the valence and dipole bound anionic states respectively. We have performed a series of multilayer calculations assuming the uracil moiety as the main fragment and the water molecule as its environment. Different combinations of settings have been used for the main fragment, environment-fragment and the inter-fragment region. Possible lower level treatment includes EA-EOM-DLPNO-CCSD with less tight threshold or the simple HF method neglecting all the correlation contribution. The results obtained from different multilayer methods are presented in Table 1. All the calculations are performed using aug-cc-pVDZ basis set with additional 5s5p4d functions added to the positive end of the dipole.

Table 1: VDE of monohydrated uracil obtained from different settings of multi-layer EA- EOM-DLPNO-CCSD method

<i>Basis set: aug-cc-pVDZ</i>	Valence bound	Dipole bound
Full TPNO	0.866	0.163
TPNO-TPNO-HF	0.850	0.160
TPNO-NPNO-HF	0.849	0.160
TPNO-LPNO-HF	0.847	0.160
TPNO-HF-HF	0.846	0.160
QM-MM	0.847	0.174

The VDE of valence bound (VB) and dipole bound (DB) anions from the full EA-EOM-DLPNO-CCSD calculation on the monohydrated system are found to be 0.866 eV and 0.163 eV, respectively. The VDE of VB and DB anion slightly decreases when we describe the water molecule at HF level, keeping the main fragment and inter-fragment interaction fixed at TIGHTPNO. The change in the VDE for both the VB and DB state is negligible as the inter-fragment description progressively goes down from TIGHTPNO to NORMALPNO to LOOSEPNO and then to HF.

We also performed a QM/MM calculation for the VDE of the monohydrated uracil system where the uracil moiety has been treated quantum mechanically and the water molecule is treated as a TIP3P point charge. For the VB state, it gives almost the identical result as that obtained from the multilayer calculations. The error in QM/MM method is slightly larger for the DB state. However, it should be noted that the errors

in both multi-layer EA-EOM-DLPNO-CCSD and QM/MM calculations for this particular example are within the error bar of the canonical EA-EOM-CCSD method itself.

3.1.2. DNA Model System:

In the previous subsection, we have investigated the accuracy of the multilayer EA-EOM-DLPNO-CCSD on micro-solvated uracil, a system with only fifteen atoms. We have seen from our previous experience on the multi-layer method for ionization potential⁸¹ that the conclusions drawn from the small molecules are often not transferable to the large systems, where the use of a multilayer method will be of actual importance. Moreover, in the previous model system, the environment fragments are not covalently bonded to the main fragment. To investigate the performance of the multilayer EA-EOM-DLPNO-CCSD method for bonded systems, we have chosen a DNA subunit with three base-pairs in the order A-G-A in one chain and the corresponding complementary bases T-C-T in the other chain. The model was created using software Avogadro¹¹³ and the additional negative charges were neutralized by adding hydrogen to the unsaturated phosphate group. The anion geometry is optimized using XTB method¹¹⁴, where only the cytosine coordinates are allowed to relax and the rest of the molecule is kept frozen. The final geometry of the model system is provided in the supporting information.

Electron attachment to nucleobases is a crucial step in the secondary radiation damage^{115–118} pathway of genetic materials. However, accurate wave-function based simulation of the electron attachment to genetic material is restricted at most to the base-pairs owing to the high computation cost of the calculations^{119,120}.

Figure 3: The natural orbitals corresponding to the (a) valence bound and (b) dipole bound state of the model DNA system

We calculated the VDE of the DNA model system treating the entire molecule in standard EA-EOM-DLPNO-CCSD/ma-def2-SVP method using NORMALPNO settings. We consider this result as our

benchmark VDE for the model system. The system consists of 652 correlated electrons and 2556 basis functions and the correlation calculation took 4640 minutes. We obtained two bound anionic states. One can see from Figure 3 that the natural orbital corresponding to the state-I (Figure 3(a)) is located over the cytosine base and the natural orbital corresponding to the state-II (Figure 3(b)) is delocalized away from the nuclear framework. Therefore, the state-I is valence bound and the state-II is dipole bound in nature. To investigate the effect of the DNA environment on the electron attachment to the cytosine base, we have performed three sets of multilayer calculations: (i) first taking the cytosine base as the main fragment and rest of the system as its environment, (ii) taking the cytosine and its complementary base guanine as the main fragment and rest of the system as its environment & (iii) taking the hole chain containing the cytosine base as the main fragment and the other chain as its environment. The VDE values obtained in these different multilayer calculations are then compared with the VDE obtained from the full NORMALPNO calculation. All the results, along with the time taken for the correlation calculation are presented in Table 2. It can be observed that the neglect of inter-fragment and environmental interaction leads to only one bound anionic state (state-I) and it is valence bound in nature. The delocalized dipole bound state (state-II) totally disappears in this case. Large error in the VDE is observed even for the valence bound state which is localized on the cytosine. The inclusion of inter-fragment interaction does not lead to any noticeable improvement. However, even a LOOSEPNO treatment of the environment can result in the significant improvement of the VDE values. The delocalized dipole-bound state also gets reproduced with sufficient accuracy and the computational timing is reduced to half compared to full NORMALPNO .

Table 2: VDE of the two lowest bound states of the DNA model system and the corresponding timings required for the correlation calculations (T_{Corr})

Single layer	Multilayer								
	Active region: Cytosine					Active region: GC Basepair	Active region: Whole chain		
Full NPNO	NPNO-LPNO-LPNO	NPNO-LPNO-HF	TPNO-HF-HF	NPNO-HF-HF	EF-DLPNO	NPNO-HF-HF	NPNO-HF-HF	QM/MM	
T_{corr} 4640 m	2088 m	676 m	1270 m	248 m	903 m	1026 m	1308 m	687m	
State-I 1.563	1.610	0.984	0.969	0.978	1.566	1.025	1.498	1.203	
State-II 0.210	0.247	NA	NA	NA	0.246	NA	0.195	0.059	

Increasing the size of the main fragment to the base-pair does not show any improvement in the calculated VDE values. The results significantly improve on taking the whole chain containing cytosine as the main fragment. In that case, one can neglect the inter-fragment and environmental interactions.

An interesting thing to notice that the inclusion of inter-fragment interaction leads to very little improvement of the VDE. It is in sharp contrast with that in the multi-layer implementation of IP-EOM-DLPNO-CCSD, where the inclusion of inter-fragment interaction significantly improves the accuracy⁸¹. This can be attributed to two reasons. Firstly, in the EOM-CCSD method, the $\hat{R}$ operation brings both the correlation and the orbital relaxation effect. Therefore, the truncation of the $\hat{R}_2$ operator leads to the reduction of both correlation and relaxation effect in IP- and EA-EOM-DLPNO-CCSD. Now, in the case of ionization, the correlation and the relaxation effect tend to cancel each other to a large extent. Therefore, the error introduced by multi-layer truncation is generally small in the case of IP-EOM-DLPNO-CCSD method⁸¹. However, in the case of the EA, the error due to missing correlation and relaxation effects reinforces each other, leading to higher truncation error in the multi-layer EA-EOM-DLPNO-CCSD method. Secondly, if a particular orbital is not localized on the main fragment, then all the contribution up to second-order involving that particular orbital in EA-EOM-DLPNO-CCSD get automatically neglected even when one includes the inter-fragment interaction term. The terms beyond second order in perturbation generally has a small contribution in the calculated EA (as discussed in section 2.3). Therefore, to get sufficient accuracy one needs to have at least a LOOSEPNO treatment of the environment interactions.

Figure 4: The explicit fragmentation scheme for DNA model system. Six different colors denote the six different fragments

In the case of EF-DLPNO calculation on the DNA model system the molecule is divided into six hypothetical fragments following the scheme suggested by Jensen and co-workers¹²¹. A pictorial representation of the fragments is presented in Figure 4. The fragment containing the cytosine is treated as

the main fragment. It can be seen that the EF-DLPNO method gives very good agreement with the reference EA-EOM-DLPNO-CCSD and requires much less computational time than the multi-layer EA-EOM-DLPNO-CCSD with NPNO-LPNO-LPNO setting.

We have also performed the EA-EOM-DLPNO-CCSD based QM/MM calculation on DNA model system by treating the whole chain containing the cytosine in the QM region and the other chain is treated with MM. The forcefield is generated using ORCA forcefield utility. The VDE for state-I in QM/MM is underestimated by 0.36 eV whereas the state II shows a large error. Therefore, the QM/MM calculations may be more economical in terms of computational cost but much less accurate than the multi-layer EA-EOM-DLPNO-CCSD with NPNO-LPNO-LPNO setting or EF-DLPNO method.

3.2. Vertical Electron Affinity:

To investigate the performance of the multi-layer method on VEA, we have studied the electron attachment to quinone in the photosynthetic reaction center (RC) from Rhodobacter Sphaeroides in the charge-neutral $DQ_A Q_B$ state¹²². The PDB structure of the RC is taken from the protein data bank¹²³ (PDB ID: 1AIJ). Our focus is on the terminal electron acceptor Q_B , which is a ubiquinone molecule. We have constructed the model system by cutting out the quinone molecule along with its immediate neighboring amino acids and discarded the rest of the RC. The position of the hydrogens is optimized using XTB. The geometry of the final model compound is provided in the supporting information. First, a full EA-EOM-DLPNO-CCSD calculation is performed on the whole system using TIGHTPNO settings and ma-def2-SVP basis set, which is taken as the reference value for the multi-layer model. The correlation calculation took 14497 minutes. We have obtained two bound states and the natural orbital corresponding to them is plotted in Figure 5. The natural orbital corresponding to the lowest energy bound state is found to be located on the molecular framework of quinone (state-I) while that of the other one is located away from the nuclear framework of quinone (state-II). We have considered the quinone molecule as the central fragment while the rest of the system is considered as its environment for the multi-layer calculations. A multi-layer EA-EOM-DLPNO-CCSD calculation using TIGHTPNO setting for the main fragment and LOOSEPNO for inter-fragment and environmental interaction gives very good agreement with the benchmark values. The errors are as small as 0.003 eV and 0.059 eV for state-I and state-II, respectively. The time required for the multi-layer calculation is fivefold less than that of the standard EA-EOM-DLPNO-CCSD method with TIGHTPNO settings. The same trend is observed for the NORMALPNO treatment of the main fragment and LOOSEPNO treatment of the inter-fragment and environmental interaction, where the error for state-I and state-II are 0.032 and 0.059 eV, respectively. The reduction in the time required for the correlation calculation, in this case, is 28 fold as compared to the benchmark calculation. The complete neglect of the inter-fragment interaction leads to large errors in the VEA for state-II (Table S1). We have also performed

an EF-DLPNO calculation where each of the amino acids is considered as a separate fragment. The quinone moiety itself is treated as the main fragment. The EF-DLPNO method shows an even higher speed-up (55 fold) with a slight increase in the error for state-I. Figure 6 presents the errors in the peak separation between the state-I and state-II with respect to benchmark values. It can be seen that the error in the peak separation in the multi-layer EA-EOM-DLPNO-CCSD method with both TPNO-LPNO-LPNO and NPNO-LPNO-LPNO is less than 0.05 eV. The peak separation error in EF-DLPNO method is slightly higher at 0.17 eV.

Figure 5: The natural orbitals corresponding to (a) state-I and (b) state-II of the Q_B model system. The quinone is denoted with ball and stick model

However, they are much more accurate than the QM/MM result, where quinone is considered as QM and the environment is treated with MM using CHARMM compatible forcefields. We have found that, although the state-I is reasonably reproduced in QM/MM method, the state-II is severely underestimated. It results in a large error of 1.1 eV in the peak separation.

Table 3: The VEA corresponding to the two lowest bound states of Q_B model system and corresponding computational timings

<i>Basis set:</i>										
<i>ma-def2-SVP</i>	Full TPNO		TPNO-LPNO-LPNO		NPNO-LPNO-LPNO		EF-DLPNO		QM/MM	
T_{tot}	14604 m		2861 m		625 m		366 m		24 min	
T_{corr}	14497 m		2732 m		517 m		262 m			
State	I	II	I	II	I	II	I	II	I	II
VEA	2.939	1.276	2.942	1.335	2.971	1.335	3.119	1.287	3.144	0.380

Figure 6: The errors in peak separation between the first two bound states of quinone with respect to the full EA-EOM-DLPNO-CCSD/ma-def2-SVP method with TIGHTPNO setting

3.3. Adiabatic Electron Affinity of GC Base Pair:

AEA is more challenging to calculate in an approximate method compared to the VDE or VEA. For the latter two, the energy of the neutral and anion species is calculated at the same geometry, which leads to better error cancellation. However, in the case of AEA, the neutral and the anion energy are calculated at their respective optimized geometries. Consequently, one needs to have a proper balance in the truncation of the neutral and anion state wave-function to get quantitative accuracy, which is difficult to achieve as the nature of the neutral and the anionic state is fundamentally different. Therefore, most of the multi-layer quantum chemical (and QM/MM) calculations focus solely on the vertical energy differences.

To investigate the performance of the multi-layer EA-EOM-DLPNO-CCSD method, we took a guanine-cytosine nucleic acid base pair (GC). The neutral and the anion geometry were optimized using B3LYP/6-31G ++ (d,p) method.

The EA-EOM-DLPNO-CCSD calculations are then performed using aug-cc-pVTZ basis set with an additional 5s5p4d diffuse function added to the positive end of the dipole. The electron attachment to GC base-pair leads to two bound anionic states¹²⁰. The first one is a dipole bound state which is vertically bound. The second bound anionic state is valence bound in nature, and it is bound adiabatically. The EA-EOM-DLPNO-CCSD natural orbitals in Figure 7 shows the additional electron corresponding to the

valence bound state is localized on cytosine. The cytosine is considered as the main fragment in multi-layer EA-EOM-DLPNO-CCSD calculation, and the results corresponding to different truncation thresholds are presented in Table 4. For the QM/MM calculation, the cytosine is taken in the QM region and guanine is treated with MM. A CHARM compatible forcefield has been used for the MM part. The full NORMALPNO treatment gives an AEA value of 0.118 eV, which is taken as the benchmark. The AEA value gets reduced to half of the benchmark value when the environment and inter-fragment interactions are completely neglected. The inclusion of inter-fragment interaction actually leads to the deterioration of results. A LOOSEPNO treatment of the inter-fragment and environmental interaction does not show any appreciable improvement in AEA value. The EF-DLPNO method also fails to provide any appreciable result. One at least needs to treat the inter-fragment interaction at NORMALPNO and environmental interaction at LOOSEPNO level to get acceptable accuracy. Therefore, the multi-layer EA-EOM-DLPNO-CCSD methods cannot give quantitative accuracy for AEA. However, the results are much more accurate than a standard QM/MM calculation which shows an AEA value of 0.434 eV.

Figure 7: EA-EOM-DLPNO-CCSD natural orbital corresponding to the valence bound anionic state in GC base pair

Table 4: AEA of GC basepair in different approximations of the EA-EOM-DLPNO-CCSD/aug-cc-pVTZ+5s5p4 method

Method	AEA (in eV)
Full NPNO	0.118
NPNO-HF-HF	0.067
NPNO-NPNO-HF	0.002
NPNO-LPNO-LPNO	0.036
NPNO-NPNO-LPNO	0.082
EF-DLPNO	0.006

3.4. Potential Energy Surface:

The electron attachment to adenine-thymine (AT) base-pair gives rise to two kinds of anions similar to GC: one is a dipole bound state, which is vertically bound and another is a valence bound state which is bound adiabatically. Figure 8 represents the natural orbital corresponding to the valence and dipole bound state of AT base pair.

Figure 8: EA-EOM-DLPNO-CCSD natural orbital corresponding to the (a) valence and (b) dipole bound anionic state in AT basepair

The electron attachment to AT base pair in the gas phase happens through a doorway mechanism. The initial electron attachment leads to the formation of the dipole bound state, which then gets converted into a valence bound state through the mixing of electronic and nuclear degrees of freedom^{124–126}. Figure 9 presents the adiabatic potential energy surface (PES) corresponding to the ground and first excited state of the AT anion along a linear transit from the dipole bound to valence bound geometry in different approximations to the EA-EOM-DLPNO-CCSD method. The aug-cc-pVTZ basis set with additional 5s5p4d functions placed at the positive end of the dipole has been used for the calculations. The intermediate geometries are generated using the following expression

$$\mathbf{R} = (1-\lambda) \mathbf{R}_{\text{DB}} + \lambda \mathbf{R}_{\text{VB}} \quad (36)$$

where $\mathbf{R}$ is the geometrical parameter (bond length, bond angle and dihedral) at the intermediate geometry, the $\mathbf{R}_{\text{DB}}$ is the geometrical parameters at dipole bound geometry and $\mathbf{R}_{\text{VB}}$ is the geometrical parameters at the valence bound geometry. The value of λ varies from 0 to 1. Setting $\lambda=0$ gives rise to dipole bound geometry while $\lambda=1$ leads to valence bound geometry. The lowest energy value in each method has been scaled to zero for the representation purpose. It can be seen from Figure 9 that the valence bound state, in the multi-layer EA-EOM-DLPNO-CCSD and EF-DLPNO method, becomes progressively

less stabilized form the dipole-bound to the valence bound geometry, which is consistent with our observation in case of AEA. One can see that the adiabatic potential energy surfaces corresponding to the ground and the first excited state of the anion in all the methods exhibit an avoided crossing, which indicates the breakdown of the Born-Oppenheimer approximation. In such cases, one needs to use the so-called diabatic basis which substitutes the electron-nuclear coupling by electronic coupling. We have used the valence bound and dipole bound nature of the state as the diabatic basis and calculated the coupling element between the two diabatic surfaces by fitting a simple avoided crossing model potential (Figure 10)

$$V = \begin{pmatrix} V_1 & W \\ W & V_2 \end{pmatrix} \quad (37)$$

where the diagonal elements are defined by the harmonic potential

$$V_i = \frac{1}{2} \omega_i (\lambda - \lambda_i^0)^2 + v_i^0 \quad (38)$$

And the off-diagonal elements are assumed to be constant. One can also calculate the rate of transition of the electron from the dipole bound to the valence bound state using the Marcus formula¹²⁷

$$k = \frac{2\pi}{\hbar} |W|^2 \sqrt{\frac{1}{4\pi k_B T \lambda_R}} e^{-\frac{(\lambda_R + \Delta G^0)^2}{4\lambda_R k_B T}} \quad (39)$$

Figure 9: The adiabatic potential energy surface corresponding to the ground and first excited state of AT base pair anion in single-layer and different approximations to the multi-layer EA-EOM-DLPNO-CCSD

The rate of transition from the dipole-bound to the valence bound state in the standard EA-EOM-DLPNO-CCSD method with NORMALPNO setting is $3.37 \times 10^{11} \text{ sec}^{-1}$. The rate obtained in multi-layer EA-EOM-CCSD-DLPNO with NPNO-LPNO-LPNO setting is two orders of magnitude less at $7.9 \times 10^9 \text{ sec}^{-1}$. The rate in the EF-DLPNO method is even lower at $2.42 \times 10^9 \text{ sec}^{-1}$. The valence bound state in both multi-layer EA-EOM-CCSD-DLPNO and EF-DLPNO is much less stabilized as compared to that of the standard EA-EOM-DLPNO-CCSD method, which leads to a lower rate of electron transfer from the dipole bound to valence bound state. Therefore, the multi-layer EA-EOM-DLPNO-CCSD methods cannot give quantitative accuracy for potential energy surfaces of anions.

Figure 10: The diabatic potential energy surface corresponding to the dipole and valence bound surface of AT base pair anion in standard EA-EOM-DLPNO-CCSD method

3.5. Computational Timing:

From the VDE and VEA studies in the previous subsections, we have seen that the use of multi-layer EA-EOM-DLPNO-CCSD can give significant computation advantage over standard EA-EOM-DLPNO-CCSD method. To understand the systematic trend in the reduction of computation time in the multi-layer EA-EOM-DLPNO-CCSD method, we have taken a series of thymine-(glycine)_n cluster, with n= 1 to 5. The motivation behind choosing such a system is that, some specific proteins are known to stabilize the anionic state of DNA by hydrogen bonding and prevent the radiation-induced DNA strand breaking^{128,129}. DNA nucleobase thymine, solvated by amorphous glycine, is protected from radiation damage by formation of

H-bonding with the glycine which stabilizes the excess electron captured by thymine. Glycine can also act as an electron scavenger by directly capturing the excess electron itself.

The geometries of the thymine-(glycine)_n anion are optimized using RI-BP86/6-31G* level of theory. The optimized geometries are provided in the supporting information.

Figure 11: EA-EOM-DLPNO-CCSD natural orbital corresponding to the valence bound anionic state in $\text{Thy}-(\text{Gly})_n$ clusters

The single point EA-EOM-DLPNO-CCSD calculations are performed using an ma-def2-TZVP basis set and the thymine is considered as the main fragment in multi-layer calculations. From Figure 11 one can see that the lowest energy anionic state in all the clusters is valence bound in nature and the extra-electron is localized on thymine. The VDE and the time taken by the correlation module are presented in Table S2. As the multi-layer EA-EOM-DLPNO-CCSD with TPNO-LPNO-LPNO setting and the EF-DLPNO calculations can provide sufficient accuracy in VDE, the timings for only these two methods are compared with full calculation. Figure 12 shows that the time required for the correlation calculation rises less steeply in the multi-layer EA-EOM-DLPNO-CCSD method than that in the standard variant. The timing advantages are even higher in the EF-DLPNO method than that in the multi-layer EA-EOM-DLPNO-CCSD method.

The error in VDE in multi-layer and EF-DLPNO method with respect to the standard EA-EOM-DLPNO-CCSD is plotted in Figure 13. One can see that the error in both multi-layer and EF-DLPNO

method is quite small and less than 0.015 eV. Although there is no systematic trends in the results, it is gratifying to note that the error does not increase with an increase in the system size.

Figure 12: Increase in the time taken in the correlation calculation in standard, multi-layer, and EF-DLPNO EA-EOM-DLPNO-CCSD method

Figure 13: The error in VDE in multi-layer and EF-DLPNO method compared to the standard EA-EOM-DLPNO-CCSD with increasing no of glycine molecules

4. Conclusion:

In this study, we have presented the implementation and benchmarking of a multi-layer EA-EOM-DLPNO-CCSD method. The method can treat environmental effects of both bonded and non-bonded nature. It allows the mutual polarization of the main fragment and the environment during the electron attachment process and can describe anionic states with both localized and delocalized electron density.

The complete neglect of environment interaction leads to significant errors in the multi-layer EA-EOM-DLPNO-CCSD method, which is in contrast with the IP variant where the environmental interactions are shown to be not so important⁸¹. However, even a LOOSEPNO treatment of the environmental interaction leads to an accuracy comparable to the standard EA-EOM-DLPNO-CCSD method for VDE and VEA. The multi-layer EA-EOM-DLPNO-CCSD method with NPNO-LPNO-LPNO setting leads to several fold speed-up with respect to the standard EA-EOM-DLPNO-CCSD method with very little loss in accuracy. We have also developed an explicit fragment version of the EA-EOM-DLPNO-CCSD method, where the entire molecule is explicitly divided into several fragments and the interaction among the different fragments is neglected. The resulting EF-DLPNO method shows even larger reduction in the computational cost as compared to the multi-layer EA-EOM-DLPNO-CCSD method with almost similar accuracy. Both the multi-layer EA-EOM-DLPNO-CCSD and EF-DLPNO method cannot give quantitative accuracy for AEA or potential energy surfaces. However, the results are in much better agreement with the benchmark values than that observed for the QM/MM based method. Therefore, for accurate simulation of electron attachment induced phenomenon, one needs to combine the multi-layer DLPNO and QM/MM method. It will allow one to have a much larger QM region in the QM/MM calculations and will remove many of the artifacts associated with the standard QM/MM calculations. Work is in progress towards that direction.

Supporting Information:

The Supporting Information is available

Cartesian coordinates of all the examples used, ORCA EF-DLPNO input file for DNA and quinone model system, additional results on quinone model systems and the timing data for the thymine-(glycine)_n clusters are provided in the supporting information.

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Supporting Information

A Multi-layer Approach to the Equation of Motion Coupled-Cluster Method for Electron affinity

Soumi Haldar¹, Achintya Kumar Dutta¹

¹Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India

▪ Optimized geometry of monohydrated uracil system:

C	-0.38641544862718	1.75686793631220	-0.09535289150661
C	0.75736749257069	0.95299449730829	-0.34941984071355
C	0.66645867328888	-0.43227805417882	-0.46240098476578
C	-1.75255659142815	-0.28030746589438	0.17689016343378
N	-1.55764786320432	1.05827427930401	0.32176967601147

newgto

S 8

1	9046.0000000	0.0007000
2	1357.0000000	0.0053890
3	309.3000000	0.0274060
4	87.7300000	0.1032070
5	28.5600000	0.2787230
6	10.2100000	0.4485400
7	3.8380000	0.2782380
8	0.7466000	0.0154400

S 8

1	9046.0000000	-0.0001530
2	1357.0000000	-0.0012080
3	309.3000000	-0.0059920

4	87.7300000	-0.0245440
5	28.5600000	-0.0674590
6	10.2100000	-0.1580780
7	3.8380000	-0.1218310
8	0.7466000	0.5490030
S 1		
1	0.2248000	1.0000000
S 1		
1	0.0612400	1.0000000
S 1		
1	0.0191375	1.0000000
S 1		
1	0.0059805	1.0000000
S 1		
1	0.0018689	1.0000000
S 1		
1	0.0005840	1.0000000
S 1		
1	0.0001825	1.0000000
P 3		
1	13.5500000	0.0399190
2	2.9170000	0.2171690
3	0.7973000	0.5103190
P 1		
1	0.2185000	1.0000000
P 1		
1	0.0561100	1.0000000
P 1		

1 0.0175344 1.0000000

P 1

1 0.0054795 1.0000000

P 1

1 0.0017123 1.0000000

P 1

1 0.0005351 1.0000000

P 1

1 0.0001672 1.0000000

D 1

1 0.8170000 1.0000000

D 1

1 0.2300000 1.0000000

D 1

1 0.0719750 1.0000000

D 1

1 0.0224609 1.0000000

D 1

1 0.0070190 1.0000000

D 1

1 0.0021934 1.0000000

end

NewAuxGTO "AutoAux" end

N -0.63739965416493 -0.96370937413863 -0.24035767512473

H -2.41248505777808 1.56498361733596 0.46798622985409

H -0.71163706627312 -1.96669310457445 -0.26347728487918

H -0.28429241445647 2.73355521929104 0.36407417614933

H 1.71260333692287 1.41121411045519 -0.54950901342845

O	-2.83317626125925	-0.83700560289344	0.40142049791344
O	1.55811011235493	-1.28227958753467	-0.72854358410901
H	3.09163243041321	-0.65424012755456	-0.17787847229303
O	3.85112003969333	-0.21171821226622	0.26881099899277
H	3.38009736107191	0.37235012185024	0.86725386941822

▪ **Optimized geometry of DNA double-helix model system:**

H	-5.632	8.586	-0.713
O	-5.137	8.216	0.073
C	-6.077	7.969	1.148
H	-6.714	7.252	0.865
H	-6.459	8.841	1.453
C	-5.347	7.408	2.349
H	-5.969	7.583	3.234
O	-5.137	5.975	2.138
C	-3.777	5.731	1.834
H	-3.314	5.145	2.641
N	-3.727	4.934	0.580
C	-3.827	5.550	-0.643
H	-3.948	6.632	-0.691
C	-3.577	3.569	0.702
O	-3.487	3.012	1.781
N	-3.537	2.871	-0.489
H	-3.431	1.879	-0.424
C	-3.627	3.402	-1.753
O	-3.577	2.673	-2.751
C	-3.777	4.836	-1.785
C	-3.887	5.458	-3.144
H	-2.918	5.895	-3.429

H	-4.655	6.243	-3.127
H	-4.167	4.687	-3.878
C	-3.067	7.074	1.739
H	-3.113	7.398	0.794
H	-2.165	6.994	2.163
C	-3.947	7.959	2.610
H	-3.877	9.016	2.309
O	-3.557	7.818	3.970
P	-2.007	7.909	4.121
O	-1.787	8.539	5.439
O	-1.217	8.460	2.997
O	-1.757	6.336	4.225
C	-2.697	5.527	4.974
H	-3.334	5.094	4.336
H	-3.079	6.076	5.718
C	-1.967	4.387	5.649
H	-2.589	4.033	6.480
O	-1.757	3.322	4.669
C	-0.397	3.291	4.280
H	0.066	2.353	4.617
N	-0.280	3.447	2.783
C	-0.133	4.802	2.341
H	-0.860	5.480	2.848
C	0.137	4.912	0.928
H	0.108	5.898	0.427
C	0.127	2.338	2.039
O	0.201	1.219	2.618
N	0.423	2.489	0.710

C	0.398	3.756	0.172
N	0.716	3.816	-1.199
H	0.602	2.907	-1.680
H	0.199	4.548	-1.695
C	0.313	4.454	4.958
H	0.267	5.254	4.360
H	1.215	4.148	5.264
C	-0.567	4.695	6.175
H	-0.497	5.738	6.523
O	-0.177	3.812	7.220
P	1.373	3.802	7.396
O	1.593	3.581	8.840
O	2.163	4.891	6.778
O	1.623	2.444	6.596
C	0.683	1.354	6.759
H	0.046	1.356	5.989
H	0.302	1.388	7.683
C	1.413	0.031	6.674
H	0.791	-0.729	7.161
O	1.623	-0.296	5.265
C	2.983	-0.102	4.926
H	3.446	-1.068	4.675
N	3.033	0.774	3.725
C	2.933	2.137	3.853
H	2.812	2.578	4.842
C	3.183	0.161	2.500
O	3.273	-1.046	2.375
N	3.223	1.016	1.415

H	3.329	0.592	0.515
C	3.133	2.386	1.447
O	3.183	3.049	0.404
C	2.983	2.940	2.771
C	2.873	4.432	2.853
H	3.842	4.857	3.156
H	2.105	4.703	3.590
H	2.593	4.834	1.867
C	3.693	0.477	6.142
H	3.647	1.475	6.098
H	4.595	0.052	6.222
C	2.813	-0.010	7.283
H	2.883	0.656	8.157
O	3.203	-1.328	7.649
H	4.144	-1.505	7.583
H	5.777	-1.173	-8.754
O	5.283	-1.873	-8.239
C	6.223	-2.883	-7.793
H	6.862	-2.469	-7.145
H	6.602	-3.350	-8.592
C	5.493	-3.953	-7.010
H	6.116	-4.855	-7.013
O	5.283	-3.472	-5.645
C	3.923	-3.127	-5.463
H	3.461	-3.807	-4.734
N	3.873	-1.740	-4.924
C	3.733	-0.033	-3.576
N	3.883	0.490	-4.848

C	3.953	-0.558	-5.610
H	4.065	-0.504	-6.692
N	3.483	-0.240	-1.246
C	3.493	-1.555	-1.437
H	3.387	-2.153	-0.540
N	3.613	-2.237	-2.556
C	3.733	-1.398	-3.601
C	3.603	0.572	-2.308
N	3.593	1.887	-2.115
H	3.684	2.526	-2.916
H	3.495	2.268	-1.162
C	3.213	-3.291	-6.800
H	3.255	-2.424	-7.296
O	1.923	-3.830	-6.545
H	1.494	-3.499	-5.753
C	4.093	-4.308	-7.506
H	4.024	-4.222	-8.597
O	3.703	-5.623	-7.103
P	2.153	-5.787	-7.164
O	1.933	-7.202	-7.531
O	1.363	-4.789	-7.920
O	1.903	-5.588	-5.601
C	2.843	-6.171	-4.663
H	3.482	-5.464	-4.361
H	3.222	-7.007	-5.059
C	2.113	-6.614	-3.413
H	2.736	-7.361	-2.907
O	1.903	-5.448	-2.556

C	0.543	-5.060	-2.601
H	0.081	-5.213	-1.615
N	0.405	-3.578	-2.953
C	0.467	-2.478	-2.098
N	0.562	-1.102	1.137
H	0.567	-1.964	1.681
H	0.442	-0.175	1.648
N	0.539	-2.488	-0.750
C	0.512	-1.253	-0.200
N	0.442	-0.092	-0.950
H	0.440	0.832	-0.427
C	0.407	-0.021	-2.363
O	0.384	1.081	-2.934
C	0.397	-1.353	-2.959
N	0.288	-1.748	-4.285
C	0.294	-3.069	-4.244
H	0.139	-3.740	-5.107
C	-0.167	-5.949	-3.612
H	-0.125	-5.512	-4.510
O	-1.457	-6.251	-3.097
H	-1.885	-5.530	-2.628
C	0.713	-7.187	-3.623
H	0.644	-7.731	-4.573
O	0.323	-8.046	-2.549
P	-1.227	-8.216	-2.507
O	-1.447	-9.592	-2.014
O	-2.017	-7.818	-3.694
O	-1.477	-7.171	-1.328

C	-0.537	-7.124	-0.224
H	0.102	-6.369	-0.372
H	-0.157	-8.038	-0.081
C	-1.267	-6.787	1.058
H	-0.644	-7.118	1.897
O	-1.477	-5.340	1.109
C	-2.837	-5.045	0.854
H	-3.299	-4.615	1.754
N	-2.887	-4.036	-0.240
C	-3.027	-2.158	-1.336
N	-2.877	-3.150	-2.288
C	-2.807	-4.243	-1.591
H	-2.695	-5.231	-2.037
N	-3.277	-0.064	-0.293
C	-3.267	-0.723	0.862
H	-3.373	-0.106	1.746
N	-3.147	-2.013	1.087
C	-3.027	-2.680	-0.075
C	-3.157	-0.756	-1.436
N	-3.167	-0.096	-2.590
H	-3.076	-0.609	-3.478
H	-3.265	0.930	-2.596
C	-3.547	-6.349	0.519
H	-3.505	-6.494	-0.470
O	-4.837	-6.308	1.115
H	-5.265	-5.449	1.096
C	-2.667	-7.378	1.207
H	-2.736	-8.362	0.729

O	-3.057	-7.483	2.579
H	-3.998	-7.384	2.742
H	-1.435	7.980	2.183
H	1.946	4.953	5.835
H	2.086	-7.317	-8.482
H	-1.294	-10.222	-2.735

▪ **Optimized geometry of ubiquinone model system:**

N	31.18900	37.67100	23.46300
H	30.76300	38.57200	23.37900
H	31.03400	37.30400	24.38000
H	30.80900	37.04900	22.77800
C	32.62400	37.80200	23.24100
H	32.71900	38.16500	22.22600
C	33.15700	38.80200	24.24500
H	32.35300	38.97300	24.99700
H	34.00400	38.34100	24.80000
C	33.60900	40.18100	23.81200
H	34.71200	40.15600	23.63900
C	32.92100	40.66700	22.56300
H	33.24900	41.69900	22.31300
H	33.16000	40.00700	21.70200
H	31.81900	40.67800	22.70100
C	33.34100	41.09400	24.97800
H	33.66700	42.13000	24.74000
H	32.26200	41.13000	25.23000
H	33.89900	40.75200	25.87600
C	33.41000	36.49400	23.33900

O	34.23300	36.20600	22.46000
N	33.17200	35.68300	24.37100
H	32.51900	35.91400	25.09100
C	33.84200	34.40200	24.53000
H	34.90300	34.59100	24.42600
C	33.53800	33.81700	25.90000
H	33.82600	34.55400	26.68100
H	32.44200	33.65600	26.00100
N	35.59300	32.33400	25.97000
H	36.27700	33.04700	25.81000
C	34.29100	32.51700	26.11300
C	35.82800	31.07200	26.19100
H	36.82200	30.62000	26.14500
N	34.70100	30.46900	26.47500
C	33.70800	31.31700	26.44300
H	32.66400	31.07800	26.60900
C	33.45400	33.38300	23.46300
O	32.79400	33.80100	22.83900
O	33.94900	32.53000	23.63200
N	35.13000	34.59000	20.17300
H	34.89100	35.54600	20.34600
H	34.78800	34.01300	20.91500
H	34.73800	34.29300	19.30200
C	36.58300	34.46800	20.10700
H	36.90300	35.06500	19.26300
C	37.23600	34.95800	21.41200
H	36.77900	35.94400	21.65900
H	36.95100	34.27100	22.23900

C	38.77000	35.15500	21.45000
H	39.26800	34.15800	21.38400
C	39.24000	36.06700	20.32000
H	40.33600	36.23800	20.38800
H	39.01800	35.61100	19.33100
H	38.73100	37.05300	20.37400
C	39.15800	35.78500	22.76900
H	40.26000	35.91800	22.82400
H	38.69200	36.78200	22.90000
H	38.84400	35.13800	23.61700
C	37.01500	33.03700	19.84600
O	36.20200	32.46000	19.77100
O	38.01400	33.00000	19.80900
N	42.33800	40.21800	21.29200
H	41.64100	39.54500	21.04500
H	43.15900	39.75300	21.62200
H	42.56200	40.78400	20.49800
C	41.82300	41.06500	22.34300
H	40.97800	41.58600	21.90900
C	41.40600	40.20800	23.52800
H	41.55800	39.13600	23.27300
H	42.03300	40.42500	24.41900
C	39.92800	40.46000	23.77200
C	38.97400	39.89500	22.91700
H	39.29400	39.24500	22.11400
C	37.62600	40.18200	23.10800
H	36.88300	39.74700	22.45400
C	37.22500	41.02400	24.14400

H	36.17600	41.23800	24.29000
C	39.52900	41.30000	24.81400
H	40.27000	41.74600	25.46200
C	38.17400	41.58200	24.99700
H	37.86400	42.23500	25.80100
C	42.81800	42.12000	22.78200
O	43.65600	42.02100	22.24500
O	42.40800	42.67300	23.50700
N	41.29800	45.89200	22.73900
H	40.46200	45.78900	22.19900
H	41.65500	44.99200	22.98900
H	41.98300	46.39700	22.21400
C	40.99100	46.63100	23.94800
H	40.64400	47.60500	23.62600
C	39.80900	45.83800	24.59800
H	39.20100	45.39900	23.76900
C	40.30300	44.70700	25.48600
H	39.44400	44.18800	25.96300
H	40.86700	43.94700	24.90600
H	40.95900	45.09900	26.29300
C	38.94000	46.82200	25.35200
H	38.10600	46.29700	25.86500
H	39.53700	47.36300	26.11800
H	38.49200	47.57100	24.66600
C	42.20000	46.85200	24.85900
O	43.00500	46.43300	24.43900
O	41.91000	47.36500	25.66600
N	43.98100	44.32500	26.51400

H	44.37600	45.19800	26.79800
H	43.01500	44.44600	26.28700
H	44.47600	43.96900	25.72100
C	44.09500	43.37400	27.61000
H	45.14800	43.19500	27.78900
C	43.34400	43.89800	28.86400
H	43.82000	44.84400	29.20500
H	42.28500	44.13200	28.61900
C	43.35700	42.96800	30.07800
C	44.55800	42.62500	30.70600
H	45.48900	43.04500	30.35100
C	44.56200	41.72800	31.77300
H	45.48800	41.45200	32.25600
C	43.35900	41.18100	32.21000
O	43.35300	40.26100	33.23600
H	42.43700	40.06000	33.43700
C	42.15700	42.42000	30.53100
H	41.23000	42.65800	30.02800
C	42.15600	41.52500	31.60100
H	41.22600	41.09000	31.93500
C	43.48900	42.06000	27.15200
O	42.65500	42.02700	26.24600
N	43.95300	40.95700	27.72200
H	44.74000	40.94200	28.33800
C	43.35200	39.66200	27.49800
H	42.32900	39.80400	27.17600
C	44.19900	38.83000	26.55800
H	44.20900	39.33300	25.56400

H	45.25300	38.79200	26.91600
O	43.63900	37.53300	26.42400
H	44.06500	37.11800	25.66300
C	43.30800	39.01100	28.86700
O	44.34500	38.89600	29.52000
N	42.14900	38.58100	29.37100
H	41.26100	38.65200	28.92100
C	42.10500	37.94600	30.68200
H	42.80100	38.49200	31.30600
C	40.63800	38.07700	31.22800
H	40.37300	39.15200	31.06200
C	39.69700	37.10300	30.54300
H	38.64400	37.31300	30.82400
H	39.77400	37.18800	29.43900
H	39.93000	36.05600	30.83100
C	40.64600	37.83600	32.73200
H	40.94200	36.78400	32.94300
H	41.41400	38.49400	33.19900
C	39.30200	38.11800	33.42400
H	39.39700	37.97800	34.52300
H	38.97500	39.16300	33.23400
H	38.51300	37.42900	33.05700
C	42.60700	36.49600	30.62100
O	42.96100	35.93900	31.66100
N	42.71600	35.86300	29.44700
H	42.45800	36.29000	28.58100
C	43.22200	34.50000	29.35100
H	43.74700	34.30000	30.27500

H	43.84500	34.45900	28.46800
C	42.11800	33.45300	29.19800
O	41.23100	33.91400	29.19200
O	42.53500	32.54600	29.13800
N	38.57000	33.94000	31.42100
H	39.19100	34.61100	31.01500
H	38.85500	33.01500	31.16900
H	38.56800	34.03700	32.41600
C	37.22200	34.17500	30.91800
H	36.94700	35.15900	31.27500
C	37.24800	34.14700	29.34300
H	37.93500	34.98400	29.05900
C	37.66100	32.77200	28.83500
H	37.83000	32.79500	27.73800
H	38.60600	32.44000	29.31400
H	36.87500	32.01700	29.04900
C	35.86500	34.49600	28.78200
H	35.88500	34.44300	27.67000
H	35.13100	33.73600	29.13400
C	35.29600	35.87500	29.17000
H	34.27100	35.99900	28.75900
H	35.24300	35.98000	30.27500
H	35.92800	36.69400	28.76800
C	36.19200	33.19400	31.48400
O	36.65300	32.56200	32.10700
O	35.29300	33.40900	31.10100
N	35.61700	34.46200	34.88700
H	36.56900	34.70100	35.07600

H	35.55800	33.95100	34.03000
H	35.24700	33.91400	35.63700
C	34.83500	35.68700	34.76400
H	34.88400	36.18200	35.72500
C	35.34500	36.59200	33.63500
H	36.41200	36.82400	33.85600
H	35.34700	36.01700	32.68300
C	34.64100	37.94500	33.38000
H	33.57000	37.75500	33.12900
C	34.72900	38.83000	34.61900
H	34.26600	39.82100	34.42400
H	34.19800	38.36000	35.47400
H	35.78800	38.99300	34.91000
C	35.28700	38.63000	32.19200
H	34.78100	39.59700	31.98200
H	36.35900	38.84400	32.37600
H	35.20800	37.99200	31.28500
C	33.37900	35.39000	34.47600
O	33.25200	34.39900	34.42900
O	32.88000	36.25300	34.39900
N	30.42800	36.67700	36.85100
H	31.33900	37.07500	36.74700
H	30.33600	35.87600	36.26000
H	30.27700	36.41600	37.80400
C	29.43300	37.66500	36.46700
H	29.53100	38.48900	37.16200
C	29.67100	38.12400	35.02800
H	29.64300	37.21500	34.38400

H	28.81600	38.75800	34.70400
C	30.97500	38.85900	34.71600
H	31.83600	38.22000	35.02600
C	31.05100	39.11800	33.21700
H	31.96700	39.69400	32.96700
H	31.07700	38.16000	32.65500
H	30.17000	39.70200	32.87400
C	31.04800	40.15800	35.49900
H	32.00400	40.68300	35.28700
H	30.22000	40.84500	35.23100
H	30.99700	39.95700	36.59100
C	28.02100	37.11400	36.60500
O	28.07000	36.17200	36.93600
O	27.36800	37.82000	36.33300
C	37.73500	40.74500	28.66700
C	38.80100	39.90200	28.30700
C	38.58900	38.71800	27.59000
C	37.28700	38.35700	27.21500
C	36.20300	39.19400	27.56700
C	36.41100	40.39800	28.28500
C	38.03900	42.00300	29.47800
C	40.15700	37.66800	25.99400
C	36.59400	37.16500	25.17800
C	35.21200	41.33000	28.53500
C	34.84300	41.34300	29.94000
C	34.14400	42.38500	30.53300
C	33.69900	43.60500	29.73200
C	33.85900	42.35000	32.02700

O	39.94900	40.21500	28.62000
O	39.67400	37.89200	27.30900
O	37.08700	37.16400	26.51400
O	35.04800	38.86100	27.26400
H	37.12900	42.53300	29.66900
H	38.70700	42.63000	28.92600
H	38.49300	41.72800	30.40700
H	40.99300	37.00100	26.03000
H	40.46100	38.59900	25.56200
H	39.38100	37.23500	25.39800
H	36.51400	36.15800	24.82700
H	37.26800	37.70900	24.55000
H	35.63000	37.62900	25.15400
H	34.37800	40.98900	27.95800
H	35.48800	42.32300	28.24700
H	35.11400	40.53800	30.52600
H	33.97100	43.47600	28.70500
H	34.17700	44.48000	30.12000
H	32.63700	43.71400	29.80900
H	33.31500	43.22800	32.30700
H	34.78300	42.31600	32.56600
H	33.27900	41.48100	32.25900

▪ **Fragmentation scheme of ORCA EF-DLPNO calculation of DNA model system:**

#multilayer input

! EA-EOM-DLPNO-CCSD NORMALPNO SP ma-def2-SVP RIJCOSX autoaux def2/J Pal2

%maxcore 50000

%mdci


```
printlevel 3

nroots 2

FollowCIS true

TCutPNOSingles 1e-12

Maxiter 2000

DToI 1e-5

NDAV 10

NormalPNOFragInter {1 1}

LoosePNOFragInter {2 2} {3 3} {4 4} {5 5} {6 6}

HFFRAGMENTINTERACTION {1 2} {1 3} {1 4} {1 5} {1 6} {2 3} {2 4} {2 5} {2 6} {3 4} {3 5}
{3 6} {4 5} {4 6} {5 6}

end
```

```
#QM/MM input
```

```
* xyz 0 1
```

```
H(2) -5.632 8.586 -0.713
```

```
O(2) -5.137 8.216 0.073
```

```
C(2) -6.077 7.969 1.148
```

```
H(2) -6.714 7.252 0.865
```

```
H(2) -6.459 8.841 1.453
```

```
C(2) -5.347 7.408 2.349
```

```
H(2) -5.969 7.583 3.234
```

```
O(2) -5.137 5.975 2.138
```

```
C(2) -3.777 5.731 1.834
```

```
H(2) -3.314 5.145 2.641
```

```
N(2) -3.727 4.934 0.580
```

```
C(2) -3.827 5.550 -0.643
```

```
H(2) -3.948 6.632 -0.691
```

```
C(2) -3.577 3.569 0.702
```

O(2)	-3.487	3.012	1.781
N(2)	-3.537	2.871	-0.489
H(2)	-3.431	1.879	-0.424
C(2)	-3.627	3.402	-1.753
O(2)	-3.577	2.673	-2.751
C(2)	-3.777	4.836	-1.785
C(2)	-3.887	5.458	-3.144
H(2)	-2.918	5.895	-3.429
H(2)	-4.655	6.243	-3.127
H(2)	-4.167	4.687	-3.878
C(2)	-3.067	7.074	1.739
H(2)	-3.113	7.398	0.794
H(2)	-2.165	6.994	2.163
C(2)	-3.947	7.959	2.610
H(2)	-3.877	9.016	2.309
O(2)	-3.557	7.818	3.970
P(2)	-2.007	7.909	4.121
O(2)	-1.787	8.539	5.439
O(2)	-1.217	8.460	2.997
O(2)	-1.757	6.336	4.225
C(1)	-2.697	5.527	4.974
H(1)	-3.334	5.094	4.336
H(1)	-3.079	6.076	5.718
C(1)	-1.967	4.387	5.649
H(1)	-2.589	4.033	6.480
O(1)	-1.757	3.322	4.669
C(1)	-0.397	3.291	4.280
H(1)	0.066	2.353	4.617

N(1)	-0.280	3.447	2.783
C(1)	-0.133	4.802	2.341
H(1)	-0.860	5.480	2.848
C(1)	0.137	4.912	0.928
H(1)	0.108	5.898	0.427
C(1)	0.127	2.338	2.039
O(1)	0.201	1.219	2.618
N(1)	0.423	2.489	0.710
C(1)	0.398	3.756	0.172
N(1)	0.716	3.816	-1.199
H(1)	0.602	2.907	-1.680
H(1)	0.199	4.548	-1.695
C(1)	0.313	4.454	4.958
H(1)	0.267	5.254	4.360
H(1)	1.215	4.148	5.264
C(1)	-0.567	4.695	6.175
H(1)	-0.497	5.738	6.523
O(1)	-0.177	3.812	7.220
P(1)	1.373	3.802	7.396
O(1)	1.593	3.581	8.840
O(1)	2.163	4.891	6.778
O(1)	1.623	2.444	6.596
C(3)	0.683	1.354	6.759
H(3)	0.046	1.356	5.989
H(3)	0.302	1.388	7.683
C(3)	1.413	0.031	6.674
H(3)	0.791	-0.729	7.161
O(3)	1.623	-0.296	5.265

C(3)	2.983	-0.102	4.926
H(3)	3.446	-1.068	4.675
N(3)	3.033	0.774	3.725
C(3)	2.933	2.137	3.853
H(3)	2.812	2.578	4.842
C(3)	3.183	0.161	2.500
O(3)	3.273	-1.046	2.375
N(3)	3.223	1.016	1.415
H(3)	3.329	0.592	0.515
C(3)	3.133	2.386	1.447
O(3)	3.183	3.049	0.404
C(3)	2.983	2.940	2.771
C(3)	2.873	4.432	2.853
H(3)	3.842	4.857	3.156
H(3)	2.105	4.703	3.590
H(3)	2.593	4.834	1.867
C(3)	3.693	0.477	6.142
H(3)	3.647	1.475	6.098
H(3)	4.595	0.052	6.222
C(3)	2.813	-0.010	7.283
H(3)	2.883	0.656	8.157
O(3)	3.203	-1.328	7.649
H(3)	4.144	-1.505	7.583
H(4)	5.777	-1.173	-8.754
O(4)	5.283	-1.873	-8.239
C(4)	6.223	-2.883	-7.793
H(4)	6.862	-2.469	-7.145
H(4)	6.602	-3.350	-8.592

C(4)	5.493	-3.953	-7.010
H(4)	6.116	-4.855	-7.013
O(4)	5.283	-3.472	-5.645
C(4)	3.923	-3.127	-5.463
H(4)	3.461	-3.807	-4.734
N(4)	3.873	-1.740	-4.924
C(4)	3.733	-0.033	-3.576
N(4)	3.883	0.490	-4.848
C(4)	3.953	-0.558	-5.610
H(4)	4.065	-0.504	-6.692
N(4)	3.483	-0.240	-1.246
C(4)	3.493	-1.555	-1.437
H(4)	3.387	-2.153	-0.540
N(4)	3.613	-2.237	-2.556
C(4)	3.733	-1.398	-3.601
C(4)	3.603	0.572	-2.308
N(4)	3.593	1.887	-2.115
H(4)	3.684	2.526	-2.916
H(4)	3.495	2.268	-1.162
C(4)	3.213	-3.291	-6.800
H(4)	3.255	-2.424	-7.296
O(4)	1.923	-3.830	-6.545
H(4)	1.494	-3.499	-5.753
C(4)	4.093	-4.308	-7.506
H(4)	4.024	-4.222	-8.597
O(5)	3.703	-5.623	-7.103
P(5)	2.153	-5.787	-7.164
O(5)	1.933	-7.202	-7.531

O(5)	1.363	-4.789	-7.920
O(5)	1.903	-5.588	-5.601
C(5)	2.843	-6.171	-4.663
H(5)	3.482	-5.464	-4.361
H(5)	3.222	-7.007	-5.059
C(5)	2.113	-6.614	-3.413
H(5)	2.736	-7.361	-2.907
O(5)	1.903	-5.448	-2.556
C(5)	0.543	-5.060	-2.601
H(5)	0.081	-5.213	-1.615
N(5)	0.405	-3.578	-2.953
C(5)	0.467	-2.478	-2.098
N(5)	0.562	-1.102	1.137
H(5)	0.567	-1.964	1.681
H(5)	0.442	-0.175	1.648
N(5)	0.539	-2.488	-0.750
C(5)	0.512	-1.253	-0.200
N(5)	0.442	-0.092	-0.950
H(5)	0.440	0.832	-0.427
C(5)	0.407	-0.021	-2.363
O(5)	0.384	1.081	-2.934
C(5)	0.397	-1.353	-2.959
N(5)	0.288	-1.748	-4.285
C(5)	0.294	-3.069	-4.244
H(5)	0.139	-3.740	-5.107
C(5)	-0.167	-5.949	-3.612
H(5)	-0.125	-5.512	-4.510
O(5)	-1.457	-6.251	-3.097

H(5)	-1.885	-5.530	-2.628
C(5)	0.713	-7.187	-3.623
H(5)	0.644	-7.731	-4.573
O(6)	0.323	-8.046	-2.549
P(6)	-1.227	-8.216	-2.507
O(6)	-1.447	-9.592	-2.014
O(6)	-2.017	-7.818	-3.694
O(6)	-1.477	-7.171	-1.328
C(6)	-0.537	-7.124	-0.224
H(6)	0.102	-6.369	-0.372
H(6)	-0.157	-8.038	-0.081
C(6)	-1.267	-6.787	1.058
H(6)	-0.644	-7.118	1.897
O(6)	-1.477	-5.340	1.109
C(6)	-2.837	-5.045	0.854
H(6)	-3.299	-4.615	1.754
N(6)	-2.887	-4.036	-0.240
C(6)	-3.027	-2.158	-1.336
N(6)	-2.877	-3.150	-2.288
C(6)	-2.807	-4.243	-1.591
H(6)	-2.695	-5.231	-2.037
N(6)	-3.277	-0.064	-0.293
C(6)	-3.267	-0.723	0.862
H(6)	-3.373	-0.106	1.746
N(6)	-3.147	-2.013	1.087
C(6)	-3.027	-2.680	-0.075
C(6)	-3.157	-0.756	-1.436
N(6)	-3.167	-0.096	-2.590

H(6) -3.076 -0.609 -3.478
 H(6) -3.265 0.930 -2.596
 C(6) -3.547 -6.349 0.519
 H(6) -3.505 -6.494 -0.470
 O(6) -4.837 -6.308 1.115
 H(6) -5.265 -5.449 1.096
 C(6) -2.667 -7.378 1.207
 H(6) -2.736 -8.362 0.729
 O(6) -3.057 -7.483 2.579
 H(6) -3.998 -7.384 2.742
 H(2) -1.435 7.980 2.183
 H(1) 1.946 4.953 5.835
 H(5) 2.086 -7.317 -8.482
 H(6) -1.294 -10.222 -2.735

*

■ **Fragmentation scheme of ORCA EF-DLPNO calculation of ubiquinone model system:**

! EA-EOM-DLPNO-CCSD NORMALPNO ma-def2-SVP RIJCOSX autoaux def2/J pal8

%maxcore 20000

%mdci

printlevel 3

nroots 2

FollowCIS true

TCutPNOSingles 1e-12

Maxiter 2000

DTOL 1e-5

NormalPNOFragInter {1 1}

LoosePNOFragInter {2 2} {3 3} {4 4} {5 5} {6 6} {7 7} {8 8} {9 9}

HFFRAGMENTINTERACTION {1 2} {1 3} {1 4} {1 5} {1 6} {1 7} {1 8} {1 9} {2 3} {2 4} {2 5}
{2 6} {2 7} {2 8} {2 9} {3 4} {3 5} {3 6} {3 7} {3 8} {3 9} {4 5} {4 6} {4 7} {4 8} {4 9} {5 6} {5
7} {5 8} {5 9} {6 7} {6 8} {6 9} {7 8} {7 9} {8 9}

end

#QM/MM input

* xyz 0 1

N(1) 31.189 37.671 23.463

H(1) 30.763 38.572 23.379

H(1) 31.034 37.304 24.380

H(1) 30.809 37.049 22.778

C(1) 32.624 37.802 23.241

H(1) 32.719 38.165 22.226

C(1) 33.157 38.802 24.245

H(1) 32.353 38.973 24.997

H(1) 34.004 38.341 24.800

C(1) 33.609 40.181 23.812

H(1) 34.712 40.156 23.639

C(1) 32.921 40.667 22.563

H(1) 33.249 41.699 22.313

H(1) 33.160 40.007 21.702

H(1) 31.819 40.678 22.701

C(1) 33.341 41.094 24.978

H(1) 33.667 42.130 24.740

H(1) 32.262 41.130 25.230

H(1) 33.899 40.752 25.876

C(1) 33.410 36.494 23.339

O(1) 34.233 36.206 22.460

N(1) 33.172 35.683 24.371

H(1)	32.519	35.914	25.091
C(1)	33.842	34.402	24.530
H(1)	34.903	34.591	24.426
C(1)	33.538	33.817	25.900
H(1)	33.826	34.554	26.681
H(1)	32.442	33.656	26.001
N(1)	35.593	32.334	25.970
H(1)	36.277	33.047	25.810
C(1)	34.291	32.517	26.113
C(1)	35.828	31.072	26.191
H(1)	36.822	30.620	26.145
N(1)	34.701	30.469	26.475
C(1)	33.708	31.317	26.443
H(1)	32.664	31.078	26.609
C(1)	33.454	33.383	23.463
O(1)	32.794	33.801	22.839
O(1)	33.949	32.530	23.632
N(2)	35.130	34.590	20.173
H(2)	34.891	35.546	20.346
H(2)	34.788	34.013	20.915
H(2)	34.738	34.293	19.302
C(2)	36.583	34.468	20.107
H(2)	36.903	35.065	19.263
C(2)	37.236	34.958	21.412
H(2)	36.779	35.944	21.659
H(2)	36.951	34.271	22.239
C(2)	38.770	35.155	21.450
H(2)	39.268	34.158	21.384

C(2)	39.240	36.067	20.320
H(2)	40.336	36.238	20.388
H(2)	39.018	35.611	19.331
H(2)	38.731	37.053	20.374
C(2)	39.158	35.785	22.769
H(2)	40.260	35.918	22.824
H(2)	38.692	36.782	22.900
H(2)	38.844	35.138	23.617
C(2)	37.015	33.037	19.846
O(2)	36.202	32.460	19.771
O(2)	38.014	33.000	19.809
N(3)	42.338	40.218	21.292
H(3)	41.641	39.545	21.045
H(3)	43.159	39.753	21.622
H(3)	42.562	40.784	20.498
C(3)	41.823	41.065	22.343
H(3)	40.978	41.586	21.909
C(3)	41.406	40.208	23.528
H(3)	41.558	39.136	23.273
H(3)	42.033	40.425	24.419
C(3)	39.928	40.460	23.772
C(3)	38.974	39.895	22.917
H(3)	39.294	39.245	22.114
C(3)	37.626	40.182	23.108
H(3)	36.883	39.747	22.454
C(3)	37.225	41.024	24.144
H(3)	36.176	41.238	24.290
C(3)	39.529	41.300	24.814

H(3)	40.270	41.746	25.462
C(3)	38.174	41.582	24.997
H(3)	37.864	42.235	25.801
C(3)	42.818	42.120	22.782
O(3)	43.656	42.021	22.245
O(3)	42.408	42.673	23.507
N(4)	41.298	45.892	22.739
H(4)	40.462	45.789	22.199
H(4)	41.655	44.992	22.989
H(4)	41.983	46.397	22.214
C(4)	40.991	46.631	23.948
H(4)	40.644	47.605	23.626
C(4)	39.809	45.838	24.598
H(4)	39.201	45.399	23.769
C(4)	40.303	44.707	25.486
H(4)	39.444	44.188	25.963
H(4)	40.867	43.947	24.906
H(4)	40.959	45.099	26.293
C(4)	38.940	46.822	25.352
H(4)	38.106	46.297	25.865
H(4)	39.537	47.363	26.118
H(4)	38.492	47.571	24.666
C(4)	42.200	46.852	24.859
O(4)	43.005	46.433	24.439
O(4)	41.910	47.365	25.666
N(5)	43.981	44.325	26.514
H(5)	44.376	45.198	26.798
H(5)	43.015	44.446	26.287

H(5)	44.476	43.969	25.721
C(5)	44.095	43.374	27.610
H(5)	45.148	43.195	27.789
C(5)	43.344	43.898	28.864
H(5)	43.820	44.844	29.205
H(5)	42.285	44.132	28.619
C(5)	43.357	42.968	30.078
C(5)	44.558	42.625	30.706
H(5)	45.489	43.045	30.351
C(5)	44.562	41.728	31.773
H(5)	45.488	41.452	32.256
C(5)	43.359	41.181	32.210
O(5)	43.353	40.261	33.236
H(5)	42.437	40.060	33.437
C(5)	42.157	42.420	30.531
H(5)	41.230	42.658	30.028
C(5)	42.156	41.525	31.601
H(5)	41.226	41.090	31.935
C(5)	43.489	42.060	27.152
O(5)	42.655	42.027	26.246
N(5)	43.953	40.957	27.722
H(5)	44.740	40.942	28.338
C(5)	43.352	39.662	27.498
H(5)	42.329	39.804	27.176
C(5)	44.199	38.830	26.558
H(5)	44.209	39.333	25.564
H(5)	45.253	38.792	26.916
O(5)	43.639	37.533	26.424

H(5)	44.065	37.118	25.663
C(5)	43.308	39.011	28.867
O(5)	44.345	38.896	29.520
N(5)	42.149	38.581	29.371
H(5)	41.261	38.652	28.921
C(5)	42.105	37.946	30.682
H(5)	42.801	38.492	31.306
C(5)	40.638	38.077	31.228
H(5)	40.373	39.152	31.062
C(5)	39.697	37.103	30.543
H(5)	38.644	37.313	30.824
H(5)	39.774	37.188	29.439
H(5)	39.930	36.056	30.831
C(5)	40.646	37.836	32.732
H(5)	40.942	36.784	32.943
H(5)	41.414	38.494	33.199
C(5)	39.302	38.118	33.424
H(5)	39.397	37.978	34.523
H(5)	38.975	39.163	33.234
H(5)	38.513	37.429	33.057
C(5)	42.607	36.496	30.621
O(5)	42.961	35.939	31.661
N(5)	42.716	35.863	29.447
H(5)	42.458	36.290	28.581
C(5)	43.222	34.500	29.351
H(5)	43.747	34.300	30.275
H(5)	43.845	34.459	28.468
C(5)	42.118	33.453	29.198

O(5)	41.231	33.914	29.192
O(5)	42.535	32.546	29.138
N(6)	38.570	33.940	31.421
H(6)	39.191	34.611	31.015
H(6)	38.855	33.015	31.169
H(6)	38.568	34.037	32.416
C(6)	37.222	34.175	30.918
H(6)	36.947	35.159	31.275
C(6)	37.248	34.147	29.343
H(6)	37.935	34.984	29.059
C(6)	37.661	32.772	28.835
H(6)	37.830	32.795	27.738
H(6)	38.606	32.440	29.314
H(6)	36.875	32.017	29.049
C(6)	35.865	34.496	28.782
H(6)	35.885	34.443	27.670
H(6)	35.131	33.736	29.134
C(6)	35.296	35.875	29.170
H(6)	34.271	35.999	28.759
H(6)	35.243	35.980	30.275
H(6)	35.928	36.694	28.768
C(6)	36.192	33.194	31.484
O(6)	36.653	32.562	32.107
O(6)	35.293	33.409	31.101
N(7)	35.617	34.462	34.887
H(7)	36.569	34.701	35.076
H(7)	35.558	33.951	34.030
H(7)	35.247	33.914	35.637

C(7)	34.835	35.687	34.764
H(7)	34.884	36.182	35.725
C(7)	35.345	36.592	33.635
H(7)	36.412	36.824	33.856
H(7)	35.347	36.017	32.683
C(7)	34.641	37.945	33.380
H(7)	33.570	37.755	33.129
C(7)	34.729	38.830	34.619
H(7)	34.266	39.821	34.424
H(7)	34.198	38.360	35.474
H(7)	35.788	38.993	34.910
C(7)	35.287	38.630	32.192
H(7)	34.781	39.597	31.982
H(7)	36.359	38.844	32.376
H(7)	35.208	37.992	31.285
C(7)	33.379	35.390	34.476
O(7)	33.252	34.399	34.429
O(7)	32.880	36.253	34.399
N(8)	30.428	36.677	36.851
H(8)	31.339	37.075	36.747
H(8)	30.336	35.876	36.260
H(8)	30.277	36.416	37.804
C(8)	29.433	37.665	36.467
H(8)	29.531	38.489	37.162
C(8)	29.671	38.124	35.028
H(8)	29.643	37.215	34.384
H(8)	28.816	38.758	34.704
C(8)	30.975	38.859	34.716

H(8)	31.836	38.220	35.026
C(8)	31.051	39.118	33.217
H(8)	31.967	39.694	32.967
H(8)	31.077	38.160	32.655
H(8)	30.170	39.702	32.874
C(8)	31.048	40.158	35.499
H(8)	32.004	40.683	35.287
H(8)	30.220	40.845	35.231
H(8)	30.997	39.957	36.591
C(8)	28.021	37.114	36.605
O(8)	28.070	36.172	36.936
O(8)	27.368	37.820	36.333
C(9)	37.735	40.745	28.667
C(9)	38.801	39.902	28.307
C(9)	38.589	38.718	27.590
C(9)	37.287	38.357	27.215
C(9)	36.203	39.194	27.567
C(9)	36.411	40.398	28.285
C(9)	38.039	42.003	29.478
C(9)	40.157	37.668	25.994
C(9)	36.594	37.165	25.178
C(9)	35.212	41.330	28.535
C(9)	34.843	41.343	29.940
C(9)	34.144	42.385	30.533
C(9)	33.699	43.605	29.732
C(9)	33.859	42.350	32.027
O(9)	39.949	40.215	28.620
O(9)	39.674	37.892	27.309

O(9)	37.087	37.164	26.514
O(9)	35.048	38.861	27.264
H(9)	37.129	42.533	29.669
H(9)	38.707	42.630	28.926
H(9)	38.493	41.728	30.407
H(9)	40.993	37.001	26.030
H(9)	40.461	38.599	25.562
H(9)	39.381	37.235	25.398
H(9)	36.514	36.158	24.827
H(9)	37.268	37.709	24.550
H(9)	35.630	37.629	25.154
H(9)	34.378	40.989	27.958
H(9)	35.488	42.323	28.247
H(9)	35.114	40.538	30.526
H(9)	33.971	43.476	28.705
H(9)	34.177	44.480	30.120
H(9)	32.637	43.714	29.809
H(9)	33.315	43.228	32.307
H(9)	34.783	42.316	32.566
H(9)	33.279	41.481	32.259

▪ **Optimized geometries of GC basepair:**

• **Neutral:**

N	4.67936	0.47473	-0.00013
C	4.97546	-0.88139	0.00047
N	3.90645	-1.63406	-0.00015
C	2.84936	-0.73871	-0.00005
C	1.43502	-0.95041	-0.00011
O	0.80606	-2.02243	-0.00018

N	0.73128	0.26963	-0.00006
C	1.29484	1.52486	0.00001
N	0.44336	2.57410	0.00002
N	2.60472	1.73235	0.00002
C	3.31174	0.58309	0.00003
H	5.99610	-1.23819	0.00068
H	-0.29876	0.18357	-0.00013
H	0.85205	3.49447	-0.00002
H	-0.57319	2.46560	-0.00009
N	-4.34545	0.91595	0.00012
C	-2.94389	1.06258	0.00001
O	-2.47258	2.20777	-0.00003
N	-2.19633	-0.07107	-0.00004
C	-2.77188	-1.28162	-0.00002
N	-1.96920	-2.35185	-0.00008
C	-4.20811	-1.43832	0.00008
C	-4.95299	-0.30331	0.00015
H	-6.03738	-0.30607	0.00022
H	-4.67324	-2.41575	0.00010
H	-0.93783	-2.23851	-0.00018
H	-2.36197	-3.27980	-0.00009
H	5.32858	1.24777	-0.00028
H	-4.87901	1.77503	0.00016

• **Anion:**

* xyz 0 1

N	4.63818	0.57343	-0.00806
C	4.99908	-0.75653	-0.17955
N	3.96461	-1.55494	-0.24531

C	2.86378	-0.72063	-0.11208
C	1.45124	-1.00671	-0.10040
O	0.89765	-2.10724	-0.21151
N	0.68676	0.16555	0.06380
C	1.19583	1.43483	0.19795
N	0.30841	2.43389	0.36629
N	2.50547	1.71246	0.18971
C	3.26199	0.61022	0.03724
H	6.03538	-1.05928	-0.24709
H	-0.37065	0.04641	0.08748
H	0.70484	3.36064	0.35056
H	-0.71421	2.31361	0.16142
N	-4.22570	0.96952	-0.36482
C	-2.85497	1.04652	-0.15039
O	-2.32977	2.19910	-0.22165
N	-2.14625	-0.06984	0.10033
C	-2.83037	-1.27635	0.19573
N	-2.02219	-2.36751	0.53255
C	-4.20530	-1.37849	0.06079
C	-4.97762	-0.21242	-0.14086
H	-5.98091	-0.22529	-0.55568
H	-4.69710	-2.34250	0.15682
H	-1.04760	-2.28736	0.23843
H	-2.42036	-3.26458	0.28859
H	5.24506	1.37496	0.07171
H	-4.68450	1.86807	-0.37906

▪ **Optimized geometries of Thymine-(Glycine)_n clusters:**

(i) Thy-(Gly)₁

N -1.11396129228557 -0.93358027963086 -3.55407596312663

C	-0.34348066536846	-0.20180140748152	-4.48306903271018
H	-0.66799426750991	-0.31087254853657	-5.51954799223705
C	0.63454479145479	1.10653770037031	-2.63250339057824
O	1.24061156427092	2.01772113154361	-2.01307401558582
N	0.02241438568207	0.05028784628259	-1.77552356954048
H	-0.06919855251017	0.33885796467506	-0.79998022714854
C	-0.97529251393864	-0.78153222571723	-2.23284173477579
O	-1.69737919140367	-1.42245370915118	-1.33269976213393
C	1.08669536369760	1.85193649427830	-4.98588558673772
H	1.67331177783620	2.59360999848332	-4.41758558048529
H	1.77147437909027	1.33980726123326	-5.69718269369343
H	0.34822070466688	2.40335218458476	-5.60901457002097
H	-1.82285772499100	-1.63534759855135	-3.88751131194974
N	-4.90422812790217	-4.77278339488560	-4.95774041815194
H	-4.63412854456081	-3.98727779660936	-5.57171373431425
C	-4.87521154681897	-4.20084827255585	-3.59926820121522
C	-3.70402805584897	-3.22580652606568	-3.31015392948644
H	-5.81827691231208	-3.64586888217816	-3.42284885292743
H	-4.85917729649207	-5.01193305181737	-2.84986526229775
O	-3.02617307411448	-2.82586306333329	-4.30064484832882
H	-4.07816326127176	-5.38553109449016	-5.02925455478680
O	-3.55924250899494	-2.89867693576345	-2.07658884408433
H	-2.49398678613590	-2.05745599259769	-1.75445200651033
C	0.43951242576098	0.89778871791417	-4.01792434717265

(ii) Thy-(Gly)₂:

N	-1.32678508137652	-0.69074415738109	-3.31412535366465
C	-0.55203621802296	0.17823455133110	-4.12843846836595
H	-0.94778394620138	0.36303823777391	-5.12844463704873

C	0.60665857821904	0.88892119820115	-2.12447752072689
O	1.54017314301142	1.57308673769858	-1.45590660000629
N	-0.17264379717461	-0.04811875822599	-1.38936794081155
H	0.02882589379158	-0.18369718640914	-0.35902113661331
C	-1.12610200777370	-0.84306971589893	-1.97499063130825
O	-1.78106331600181	-1.67978962507227	-1.27072248327215
C	1.20202565047169	2.01478359060515	-4.29337038561463
H	1.62026882433889	2.78762589235354	-3.62868301880245
H	2.05201044996184	1.54054706750389	-4.82474284670781
H	0.57666158920559	2.50877510593378	-5.06272213896409
H	-2.01397683501743	-1.33534081810921	-3.74102322571123
N	-5.20923444482177	-4.44097484812777	-5.15919019480069
H	-4.33699797183644	-4.60797214666703	-5.68057813944795
C	-4.84681815298802	-4.37043457427461	-3.73965614712900
C	-3.78051431583350	-3.31800288017025	-3.37861916679831
H	-5.75077571818505	-4.16213407465126	-3.13710458871232
H	-4.48543791504107	-5.35866667178592	-3.39978357782199
O	-3.29743966764416	-2.58497980520924	-4.26221731346611
H	-5.46144047955671	-3.48472644399283	-5.44684206241723
O	-3.48268345791140	-3.30769205646032	-2.09838163995775
H	-2.72948470659557	-2.55636215285322	-1.83721865523744
C	0.39618091384439	1.02037659282583	-3.49437347280017
N	0.34990363075919	0.02488694005161	4.07494724222311
H	-0.65782949447924	0.22208307805249	3.98201315944051
C	1.04588143401787	1.04488810690320	3.26799559869470
C	0.89010867271089	0.89516539953136	1.73077186266312
H	0.71587831397841	2.05599272047524	3.56567268949191
H	2.13109598171749	1.00279370962801	3.49320364466961

O	0.43881523328399	-0.21202462109085	1.30884395611374
H	0.44486419360973	-0.83949724455923	3.51566080609564
O	1.26313867293462	1.90331295345416	1.03414416942326
H	1.35035736060462	1.65573040861622	-0.40233980260865

(iii) Thy-(Gly)₃:

N	-1.43835116390068	-1.16054463718901	-2.85513862758778
C	-0.27981580014170	-0.74603398370787	-3.56097772216104
H	-0.14443601173109	-1.18202385175520	-4.54975435965217
C	0.48725092379220	0.29815924918522	-1.52634908630122
O	1.35811967704233	0.97681737587145	-0.76389730437498
N	-0.75039923759904	-0.05714601867250	-0.92075184264055
H	-1.00512328777881	0.41969107393885	-0.02007915487649
C	-1.70137952258097	-0.80885421686829	-1.56713686753537
O	-2.77143017449197	-1.15662087028845	-0.96566868815625
C	2.04068802921624	0.30334126056303	-3.50397913849544
H	1.95540762776514	1.20514403018741	-4.14305988440123
H	2.80404667653818	0.51285344603985	-2.73786020470011
H	2.40336595858061	-0.51951074758821	-4.14977676991934
H	-2.17218804347332	-1.71719198193034	-3.32665269947363
N	-5.84782903546701	-3.99178180059522	-5.10705609861835
H	-5.29765358520718	-3.37510210292297	-5.72216058313721
C	-5.98064985871682	-3.28789369099195	-3.82776238603662
C	-4.68486341389676	-2.66022115824119	-3.28506251650432
H	-6.72515861584619	-2.47465850163832	-3.93064513835784
H	-6.38897957214339	-3.97207373859062	-3.06276298694451
O	-3.65166233607311	-2.64262897715939	-3.97750713743487
H	-5.21304362904245	-4.78705598575788	-4.95174344186311
O	-4.82565072321169	-2.15614391673371	-2.07372072210853

H	-3.91875341273968	-1.73578116165733	-1.70126605425872
C	0.73049648595423	-0.05684987207155	-2.84808179978691
N	-1.61215756534931	0.94156225926975	4.24593725965300
H	-2.18330437350048	1.50362492569579	3.59562247583878
C	-0.23497061686219	1.07258901159759	3.74604638046962
C	-0.09502830619291	0.97472771285415	2.21331418698898
H	0.17417638869890	2.05757736424635	4.05539865409223
H	0.40405909598535	0.30512520622982	4.21267564953227
O	-1.05864538553311	1.34941250828181	1.49856099109128
H	-1.88213063254520	-0.02601470437096	4.01259619576244
O	1.04190625843211	0.51469540482168	1.76545828096038
H	1.19107053325131	0.79009972483410	0.25392161987906
N	-2.35784426799089	-3.78993614588819	1.08543042551494
H	-2.73908375596055	-3.45056060883996	1.98131399452105
C	-0.89742872765039	-3.75134890902034	1.23515491671511
C	-0.38601385039806	-2.46872546994076	1.91074053581268
H	-0.57048602188364	-4.61315432016431	1.85273300990688
H	-0.41306424847314	-3.86359394359588	0.25144333121884
O	-1.05422401297906	-1.87716322039778	2.76336645351617
H	-2.60931641530747	-3.04152825075975	0.41917526832453
O	0.82274382733899	-2.08682121900867	1.47728909253707
H	0.99360389207296	-1.11958932726999	1.78087010299138

(iv) Thy-(Gly)₄:

N	-0.66733796616470	-1.46620165776206	-3.87538543929296
C	0.25673683934636	-1.05608963805299	-4.87271017277654
H	-0.13575049350914	-1.00955250090429	-5.88948071036414
C	1.70686222565196	-0.29276623301750	-3.09674093322904
O	2.84499519792640	0.22075670652624	-2.61167344817242

N	0.75408462759165	-0.78278851539451	-2.15870841505299
H	1.00257816329352	-0.75067135038631	-1.13135740542845
C	-0.42840768136051	-1.36081642011911	-2.54143499427675
O	-1.26310285123310	-1.78514619902308	-1.66842472647594
C	2.43511125803799	0.11840029575680	-5.46739867284739
H	3.03775035486753	0.92986304675990	-5.02800811522291
H	3.14014429333332	-0.66419409889309	-5.81192905836102
H	1.91801778185321	0.50872701553963	-6.36391242722724
H	-1.55221215135952	-1.93107574985992	-4.13876431086832
N	-5.63301678893756	-4.11650908256487	-4.88510340024583
H	-5.65930524659248	-3.18950878561133	-5.33188690256643
C	-5.15733544613609	-3.91804491670437	-3.51324100354886
C	-3.81670975371050	-3.17458183832159	-3.37750406198939
H	-5.91742998463772	-3.36110566423943	-2.93439829936349
H	-5.05914364858558	-4.89732422048012	-3.00939444399793
O	-3.20985306448405	-2.76468560083484	-4.38094550772932
H	-4.88120926033614	-4.59710931766007	-5.39832283163909
O	-3.42875984350587	-3.04356855929171	-2.12068268893800
H	-2.50769335579773	-2.51894714129036	-2.03944719670011
C	1.44491131545663	-0.40662884705142	-4.45754315050851
N	1.61729438887101	0.45204511450558	3.18191723080817
H	0.86774409952413	1.12703259677865	2.96551700951646
C	2.67341362125314	0.70516269677080	2.19316288948169
C	2.32373259791027	0.39265655861983	0.71872511309673
H	2.99406651502724	1.75774873882239	2.26540276348240
H	3.56231787330716	0.09085094342688	2.44572303446291
O	1.46968956287766	-0.53137629514548	0.50836907700483
H	1.21240913534932	-0.46821101029244	2.95301203661267

O	2.94693043302135	1.05628447459845	-0.18148148410869
H	2.78241842032124	0.53904666781437	-1.61150131698344
N	-1.31054462855145	0.05581422952216	0.66451404193926
H	-0.34481486607958	-0.18578960887281	0.96938474524088
C	-2.22143726553484	0.20387529332297	1.79108362027102
C	-2.20108337169506	-0.94126105079794	2.79655152478962
H	-1.93835660219272	1.12909192878523	2.33369804588296
H	-3.25668097517400	0.35028927058723	1.43643442901899
O	-1.33451624731700	-1.79382410129550	2.91187095375775
H	-1.57321160999941	-0.69037953138214	-0.00267505630913
O	-3.29507210318602	-0.89030602163102	3.62639939934375
H	-3.15262461821754	-1.63257070936087	4.26021202954481
N	2.23083423231178	4.13484244420179	0.48384684565958
H	2.11282822498363	4.06898516798549	1.50605710933972
C	0.87398422479477	4.10143096940482	-0.08355903477392
C	-0.00493528405411	2.97090155704301	0.47973267850262
H	0.37039058937079	5.06619678912929	0.13267902130984
H	0.93537284970975	4.00100109905094	-1.17925250052251
O	0.00166925007770	2.70082300271243	1.69586627335367
H	2.68608695389908	3.24155704020825	0.22328857403258
O	-0.71858084839872	2.33127803963956	-0.43474337214696
H	-1.06929784321736	1.39588215872853	0.00256532521503

(v) Thy-(Gly)₅:

N	0.00970867367555	-3.16984905574423	-3.81025701390666
C	1.15383948517913	-3.36224251158238	-4.62951566513771
H	0.95912053247559	-3.73941276452026	-5.63185453696878
C	2.44319685353588	-2.16414396754230	-2.98051941507044
O	3.57401201486856	-1.63069041852439	-2.48551346606144

N	1.26905494635864	-2.09453844612734	-2.17135023649922
H	1.32330369857011	-1.63954645012389	-1.22153608580783
C	0.05226254948295	-2.53869416588186	-2.61373853279633
O	-1.00537681282099	-2.36032892590785	-1.90234861581558
C	3.57506140052567	-2.78249380565251	-5.13903777034846
H	4.50930696434484	-2.94462759949980	-4.57560272435249
H	3.48725745688204	-3.57423512048187	-5.90418015880520
H	3.66248602255343	-1.81083792507623	-5.66041816288749
H	-0.92242643472606	-3.49153750779267	-4.12138804637952
N	-5.33424539433177	-4.71064007220336	-5.19717614458051
H	-4.98044224067630	-4.07903681391498	-5.92860066171507
C	-5.05157686333938	-4.08365255973505	-3.90543236299751
C	-3.58076100303492	-3.71795582396403	-3.65082021288906
H	-5.65599027572835	-3.16411798558769	-3.79912874314850
H	-5.38202510241700	-4.75192748668761	-3.08830658796411
O	-2.69692901559294	-3.97252843079002	-4.48296415433571
H	-4.72261211743610	-5.53381429168645	-5.27940567580997
O	-3.39685443047572	-3.12588944969322	-2.47772809263475
H	-2.39015223340591	-2.87587927812529	-2.33209688807253
C	2.37564110965676	-2.78343072666331	-4.22328470562577
N	1.26919228677758	1.58422735865065	1.97831933355061
H	0.75063279346331	2.12993584590941	1.27294599777905
C	2.52941405188442	1.12228534811643	1.38656016072706
C	2.45933786898876	0.04221442036518	0.28030927438725
H	3.08538235768173	1.98552611598355	0.98272791665454
H	3.17075724043335	0.70173701689024	2.18876876820006
O	1.40646105638332	-0.68963169614800	0.22126628985654
H	0.68670146901161	0.75790671649641	2.17331769335521

O	3.48026663433747	-0.07693240193213	-0.46728107089412
H	3.44378225782300	-1.05175366352799	-1.61146606039844
N	-0.94262166679138	0.16862449339099	-0.65616730619851
H	-0.16037528147554	-0.01925460770585	0.04046312962864
C	-2.14335839071868	0.79695473160726	-0.06978093025353
C	-2.51186043871599	0.19235600718076	1.26681984163104
H	-1.88367405579923	1.87130184009853	0.06358105919021
H	-2.98935625020436	0.73132071282835	-0.77226973962037
O	-1.76886395904189	-0.44156852303746	2.00058401928291
H	-1.11279806930225	-0.76563372113332	-1.11313340497555
O	-3.80623051196019	0.48992220346564	1.59355529484468
H	-3.92925652853899	0.11072220281411	2.49537687275080
N	0.73861286911322	5.62471837747791	-1.38504189438671
H	-0.18696357822058	5.69412595539732	-0.93753667008682
C	0.69819057893812	4.41142865726099	-2.21182759673393
C	0.09025284124154	3.15547544567041	-1.54361138663003
H	0.11874619815170	4.61488260674879	-3.13345866698734
H	1.72082831192515	4.16720801558381	-2.55152028517911
O	-0.39087961355215	3.26104405453739	-0.38281400659563
H	1.35438979433313	5.41733781094803	-0.58612140070249
O	0.10001902524051	2.06810019529754	-2.25063639970956
H	-0.51040871035976	0.86871665560973	-1.37384888473105
N	4.46305129771620	1.05457137242488	-4.02921150298555
H	4.57417095785936	0.93075789090165	-5.04674896199668
C	3.11546357756794	1.58876488143263	-3.83838557011156
C	2.12910959580081	1.24484627466292	-4.97287806412536
H	2.71473739621191	1.26254385783676	-2.86361299245267
H	3.14828294259380	2.70090456575537	-3.79362856287436

O	2.50929228480873	0.77836123898862	-6.04542943533885
H	4.46435333645831	0.10123558653379	-3.63967597159381
O	0.83519164549036	1.56075384782645	-4.77091664874156
H	0.65946929032210	1.84243418230083	-3.80977372692378

▪ **Optimized geometries of AT basepair:**

▪ **Neutral:**

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.367491
C	1.296704	0.000000	2.047352
N	2.419148	0.000044	1.225547
C	2.439783	0.000048	-0.158785
N	1.170899	0.000025	-0.733202
H	1.154685	0.000028	-1.747273
H	-0.923724	-0.000016	-0.583384
H	-2.146622	-0.000009	1.560696
H	-1.279025	0.885714	2.854367
H	-1.279017	-0.885735	2.854346
O	3.473211	0.000071	-0.830619
N	4.934157	0.000089	2.476197
C	5.098365	0.000068	3.821328
C	6.429437	0.000095	4.314499
N	6.933796	0.000085	5.606047
C	8.257330	0.000124	5.421991
N	8.623151	0.000159	4.092708
C	7.455908	0.000141	3.350208
N	7.319540	0.000162	2.005354
C	6.022884	0.000133	1.658159
H	5.790969	0.000147	0.589573
H	9.565205	0.000191	3.716467

H	8.996090	0.000129	6.220842
N	4.012818	0.000023	4.625471
H	4.153304	0.000009	5.627107
H	3.363590	0.000060	1.695667
H	3.070244	0.000005	4.221755
O	1.417870	0.000055	3.288446
C	-1.251589	-0.000005	2.200683

▪ **Anion:**

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.419896
C	1.205802	0.000000	2.120901
N	2.402075	-0.000287	1.353055
C	2.475567	-0.000605	-0.027130
N	1.262734	-0.000329	-0.661858
H	1.323365	-0.000419	-1.671377
H	-0.885963	0.000062	-0.629572
H	-2.151540	-0.000153	1.501234
H	-1.379733	0.886383	2.848639
H	-1.379638	-0.886671	2.848593
O	3.564783	-0.000780	-0.644057
N	4.938951	-0.002183	2.929482
C	4.807705	0.000012	4.284619
C	6.014998	-0.001184	5.046866
N	6.245145	0.000494	6.418775
C	7.577795	-0.001984	6.514980
N	8.210243	-0.005025	5.289421
C	7.219146	-0.004493	4.318212
N	7.375751	-0.006623	2.975166

C	6.169100	-0.005172	2.368098
H	6.171161	-0.006772	1.274152
H	9.207999	-0.007201	5.112472
H	8.136577	-0.001670	7.449005
N	3.579577	0.003829	4.820893
H	3.516642	0.005738	5.831652
H	3.300222	-0.000341	1.851541
H	2.704893	0.005546	4.208179
O	1.340092	-0.000851	3.398585
C	-1.293070	-0.000115	2.194028

Table S1: The VEA corresponding to first two bound states of Q_B model system and corresponding computational timings

Basis set: <i>ma-def2-SVP</i>	Full NPNO		NPNO-LPNO-HF		NPNO-HF-HF	
State	I	II	I	II	I	II
	3.029	1.293	2.761	0.610	2.755	0.610

Table S2: VDE of the Thymine-(Glycine)_n cluster and the corresponding timings required for the correlation calculations (T_{Corr})

	Full TPNO	TLL	EF-DLPNO	Full TPNO		TLL		EF-DLPNO		Error in TLL (eV)	Error in EF-DLPNO (eV)
No. of Glycine around Thymine	$T_{\text{corr}}(\text{min})$	$T_{\text{corr}}(\text{min})$	$T_{\text{corr}}(\text{min})$	Root 1	Root 2	Root 1	Root 2	Root 1	Root 2	(for Root 1)	(for Root 1)
1	47	27	25	-1.161	-	-1.152	-	-1.152	-	0.009	0.009
2	67	35	39	-1.977	-	-1.984	-	-1.98	-	0.007	0.003
3	207	77	63	-2.26	-0.11	-2.261	0.113	-2.255	0.113	1E-3	0.005

4	282	89	71	- 2.263	- 0.115	- 2.254	- 0.117	- 2.249	- 0.116	0.009	0.014
5	374	129	99	- 2.488	- 0.062	- 2.493	- 0.069	- 2.488	- 0.068	0.005	0

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