CyberTraining workshop project

Non-adiabatic Molecular Dynamics of the NEU-Covalent Organic Framework with C_{60}

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Introduction

In 2020, the Lopez Lab designed a new subphthalocyanine-based 3D covalent organic framework (NEUCOF1) capable of forming cocrystals with fullerene (C_{60}) via periodic ball-and-socket binding motifs (J. Phys. Chem. C 2020, 124, 9126−9133). NEUCOF1 has a high cocrystalline surface area and long-range order that eliminates the typical surface area vs. long-range order trade-off in organic photovoltaics (OPVs). The plane-wave density functional theory calculation suggests exciton charge transfer from NEUCOF1 to the pocket-bound fullerenes, followed by a subsequent free electron transfer to the nanowire of C_{60} acceptors.

In this workshop, I plan to use CP2K to explore the hot electron relaxation process through the NECUCOF1-C_{60} donor-acceptor interface. The model creates a subsystem of NEUCOF1 (subNEUCOF1) that contains two COF shell enclosing a C_{60} molecule, shown in Figure 1.

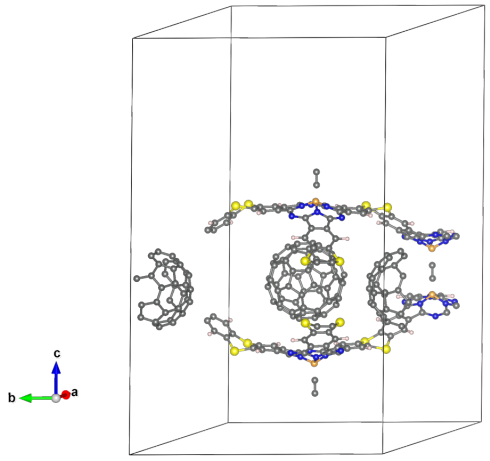

Figure 1. The 3D structure of the subsystem of NEUCOF1 with C_{60}.

Results and Discussion

The project includes 1) the convergence analysis to find optimal energy cutoff and number of grid points in electron density integration, 2) the preliminary results of the geometry optimization of the cell and nuclear positions.

I start the convergence analysis with first tuning the cutoff energy. The number of grid points, ngrids, and the relative cutoff energy, rel_cutoff were set to 6 and 150 Ry, respectively. The scan of cutoff energy cover the range from 50 to 1100 Ry in an interval of 50 Ry. The results are shown in Figure 2. The electronic energy changes dramatically as the cutoff energy decrease from 50 to 500–600 Ry suggesting inadequate cutoff energy for accurate energy evaluation. The energy

changes become less pronounce when the cutoff energy is larger than 1000 Ry. Figure 2b shows the memory usage linearly scales up with the increments of the cutoff energy. Increasing cutoff energy beyond 1100 Ry become too expensive as it requires more than 8GB per CPU. According the timing in Figure 2c, the cutoff energy below 1100Ry doubles the calculation time, while exceeding 1100 Ry substantially slow down the calculation. Therefore, the cutoff energy of 1000 Ry is a good trade-off between the calculation accuracy and efficiency.

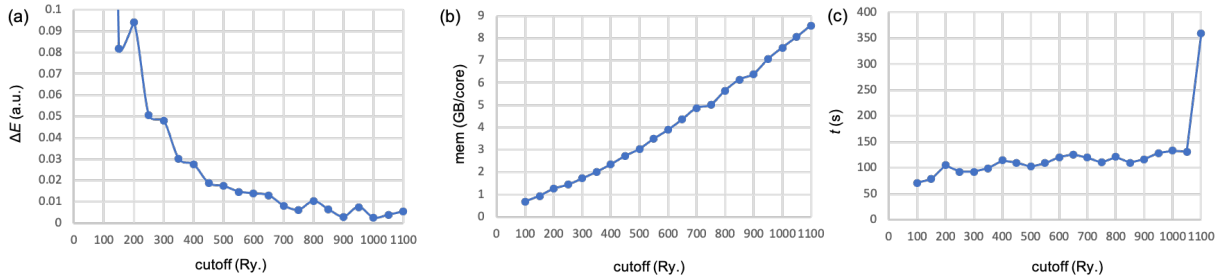

Figure 2. Convergence analysis with ngrids = 6 and rel_cutoff = 150 Ry. (a) Energy changes as the function of cutoff energy. (b) Memory usage as the function cutoff energy. (c) Computational time as the function cutoff energy.

With the cutoff energy being set, I scan the number of the grid points for electron density integration though 5 to 14. Figure 3a shows the number of grid points mainly affect the energy computed when ngrid = 4–6. When ngrid > 6, the energy difference is neglectable. Increase the ngrids also help to speed up the calculation. ngrids = 6 reduces 47% computational time of the original calculation (Figure 3b). The acceleration disappears after ngrids is larger than 6. Thus, I ngrids = 6 is the optimal choice for the energy calculation of subNEUCOF1.

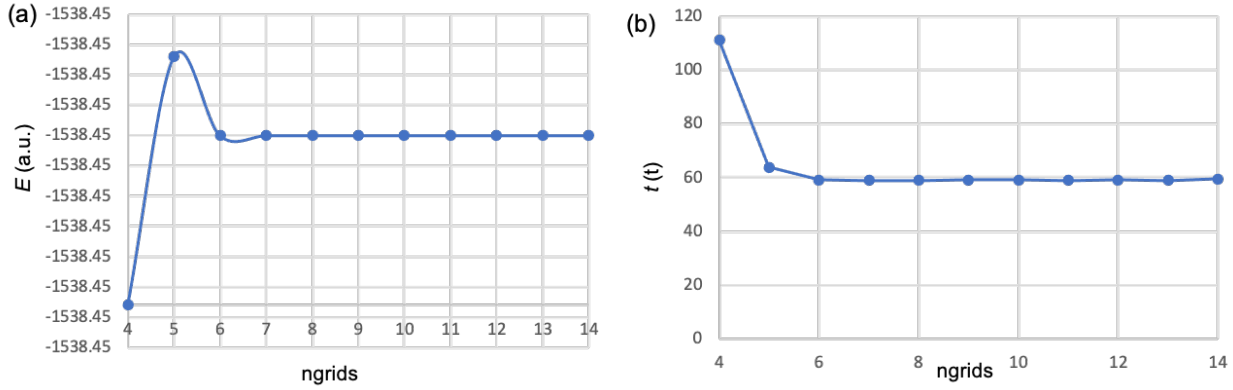

Figure 3. Convergence analysis with cutoff = 1000 Ry and rel_cutoff = 150 Ry. (a) Energy changes as the function of ngrids. (b) Computational time as the function ngrid.

CP2K uses the relative cutoff energy to partition the space to subspace for electron density integration. The scan of relative cutoff energy ranges from 50 to 150 Ry with a step size of 10 Ry. The results are collected in Figure 4. One can see the energy notably changes when the relative

cutoff energy is smaller than 60 Ry.. The dependence of energy on the rel_cutoff is less pronounced when rel_cutoff is higher than 70 Ry. We note that increasing rel_cutoff also slow down the energy calculation (Figure 4b). Considering the energy improvement of rel_cutoff = 70 Ry is 10^{-8} Hartree but increase the computational cost by 12%, I decide to use rel_cutoff = 6 for the following calculation.

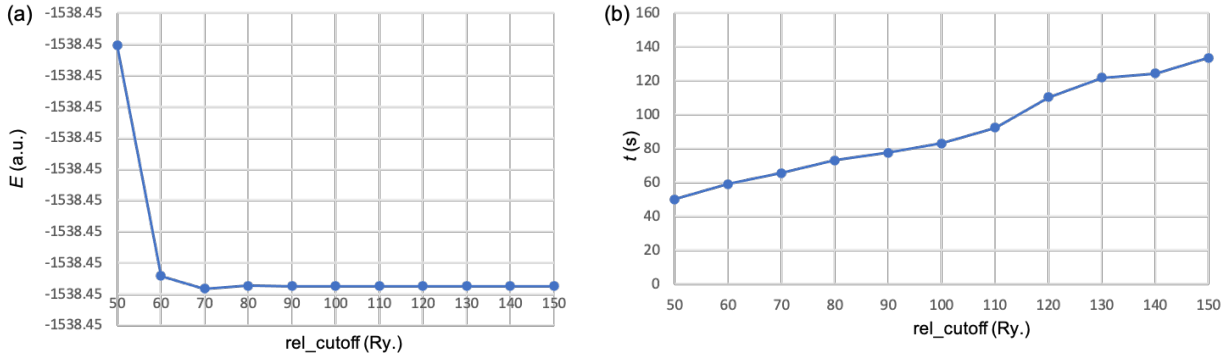

Figure 4. Convergence analysis with ngrids = 6 and rel_cutoff = 150 Ry. (a) Energy changes as the function of cutoff energy. (b) Memory usage as the function cutoff energy. (c) Computational time as the function cutoff energy.

The geometry optimization of sybNEUCOF1 relaxes the cell and nuclear position that is running parallel with 12 CPU. Figure 5 illustrates the preliminary results of the latest optimization step. The energy minimization shows an almost linear decrease. The maximum gradient quickly drops from 0.015 to 0.005 a.u./Bohr in the first 2 iteration. The root-mean-square difference of the gradients move in a constant region of 0.001–0.002 a.u./Bohr. These findings suggest the current structure lies on the descent direction of the potential energy surface and requires more step to approach the local minimum.

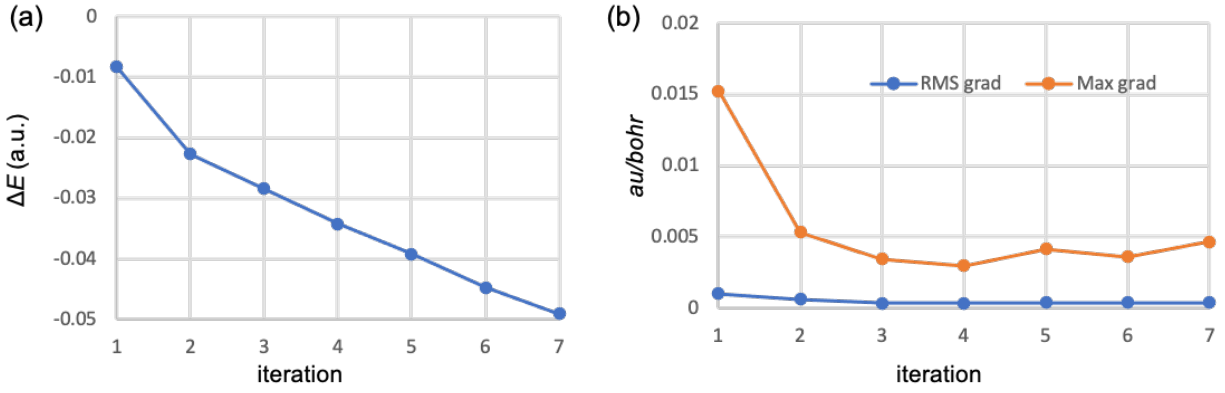

Figure 5. Geometry optimization progress of the subNEUCOF1 at PBE/DZVP-MOLOT level with GTH pseudo potential.

Remarks

I have completed the convergence analysis of using CP2K to compute electronic structure of subNEUCOF1. The parameter scan finds the optimal cutoff energy, number of grid points, and

relative cutoff energy to be 1000 Ry, 6, and 60 Ry, respectively. The cell and geometry optimization of NEUCOF1 show the latest crystal structure is approaching the local minim of the potential energy surface and the calculation require more iteration to complete.