

# Elucidation of Potent Methane Clathrate Stabilizing Agents by Means of Molecular Dynamics, Effective Fragment Potential Method and Density Functional Theory

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Storage and transportation of methane in form of methane clathrates represent promising, more ecologically-friendly and cost-efficient alternative to conventional approaches currently used in natural gas industry. The economic feasibility of methane clathrates as the methane carrier is constrained by the fact that methane clathrates are stable only at temperatures below 0°C, which leads to additional costs associated with the cooling of methane clathrates. To reduce these costs one can introduce the stabilizing agent that could be added to mixture of methane and water during crystallization of methane clathrates. Such stabilizing agent would increase the strength of binding interactions within the methane clathrate crystals and elevate the freezing point above 0°C. Moreover, the elucidation of potent and inexpensive compounds capable of increasing the freezing point of methane clathrates would not only have economic impact on natural gas industry, but also would help to resolve one of the major environmental protection problems associated with melting of natural deposits of methane clathrates.

In order to find candidate compounds, we developed methodology that combines classic force-field molecular dynamics (MD) simulations with effective fragment potential (EFP) and density functional theory (DFT) geometry optimizations. Initial step in this methodology is the DFT geometry optimization of a single cage of methane clathrate doped with the candidate compound. Upon establishing stability of the substituted cage we proceed with the DFT geometry optimization of two adjacent methane clathrate cages where candidate compound interfaces two cages. This step is followed by EFP geometry optimization of the periodic box containing doped methane clathrate cages. In case if doped structures appear stable in all of the above calculations, we proceed with the molecular dynamics simulations of direct coexistence of the solid-liquid interface, which allows us to elucidate the change in melting point of the methane clathrate upon the introduction of the candidate compound. By having the binding energies obtained from DFT and EFP calculations we correlate the change in melting point to specific interactions within the crystal structures of doped methane clathrates, which allows us not only to find potent stabilizing agents, but also explain the mechanism behind this stabilization.

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## **A TD-DFT Method for the Prediction of Electronic Response to Electron Beam Irradiation.**

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In this presentation, I will discuss our recent development efforts in the area of *ab initio* modeling of materials under electron beam irradiation. [1] The use of scanning transmission electron microscopes to manipulate substitutional defects in graphene has recently been demonstrated and modeled using ground state *ab initio* molecular dynamics, but the role of electronic excitations induced through inelastic electron scattering in promoting these transformations has so-far remained unexplored. Our recently developed methods have been applied to resolve the effects of electronic excitation on the structural dynamics of graphene quantum dots of differing edge morphologies that have been substitutionally doped with silicon or phosphorous. [2] The potential energy barriers for pyramidal inversion of these nonplanar doped species in ground and excited electronic states were evaluated using (time-dependent) density functional theory. Excited states in which the barrier is decreased are identified in the low energy region of the electronic spectrum, and the degree of barrier lowering in a given excited state is found to correlate with the extent of charge transfer away from the defect site. Transitions to these states are optically allowed, suggesting that photoexcitation can modulate the reactivity of defects in graphene under electron beam irradiation. Coupling matrix elements due to external point-source electric fields evaluated between these inversion-favoring excited states and the ground state, as well as real-time simulations of the material's response to a point charge impulse enacted immediately above the defect, indicate that focusing an electron beam near the defect can promote the population of these states. This result suggests that beam electrons incident on a defect can simultaneously excite the material to an inversion-favoring state through inelastic (beam electrons- material electrons) scattering and transfer momentum to the defect to initiate the inversion through the elastic (beam electrons- material nuclei) scattering, highlighting the importance of considering electronically non-adiabatic reaction pathways for materials under electron beam irradiation.

[1] Lingerfelt, David B., Panchapakesan Ganesh, Jacek Jakowski, and Bobby Sumpter. First Principles Determination of Electronic Excitations Induced by Charged Particles. **2019**, *ChemRxiv*. 7726139

[2] Lingerfelt, David B., Panchapakesan Ganesh, Jacek Jakowski, and Bobby Sumpter. Electronically Nonadiabatic Structural Transformations Promoted by Electron Beams. **2019**, *Adv. Funct. Mater.* (In review)

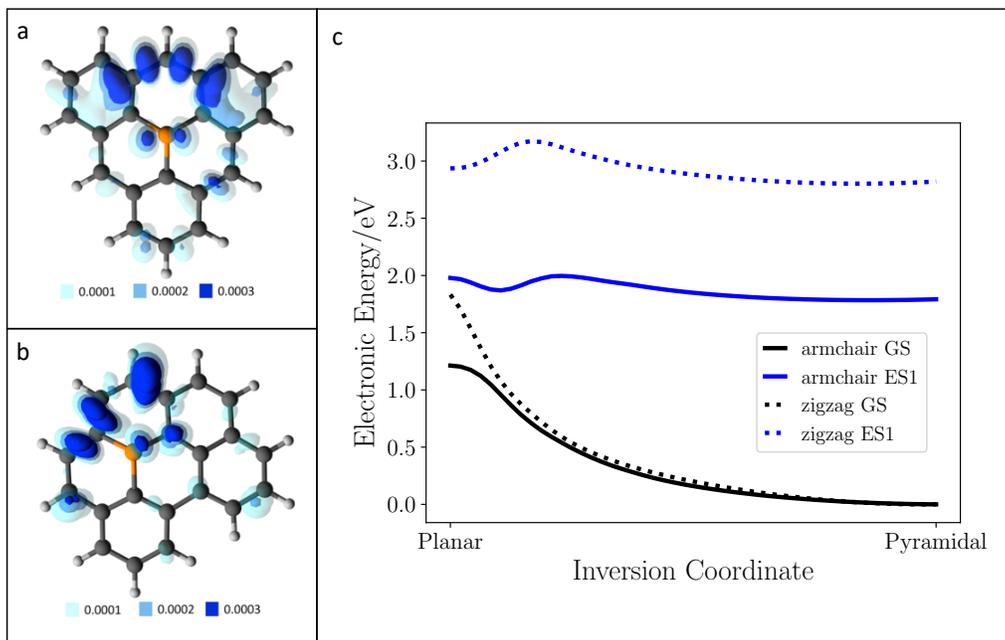


Figure 1. Potential energy surfaces for ground and first excited state along the ground state minimum energy reaction coordinate for pyramidal inversion of substitutional phosphorous defect in zigzag and armchair graphene fragments (c), and point charge locations associated with high probability for promoting transitions between ground and excited states visualized as isosurfaces of the position-dependent transition rates (a,b).

# The role of orbital angular momentum constraints in the variational optimization of the two-electron reduced-density matrix

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In order to use ab initio methods to correctly predict the properties of chemical systems containing heavy elements, one must account for both correlation and relativistic effects, including spin-orbit coupling. The complete active space self-consistent-field method (CASSCF) provides a reliable description of nondynamical correlation effects, but the steep scaling of configuration interaction (CI)-based CASSCF precludes its application to large systems. The variational two-electron reduced-density-matrix (v2RDM) driven methods provide a computationally efficient alternative to CI-based approaches. Both scalar relativistic and spin-orbit coupling effects can be captured within an exact two component (X2C) extension of v2RDM-driven CASSCF. We have developed a complex generalized implementation of the complete active space v2RDM approach (v2RDM-CASCI) that is suitable for X2C-v2RDM-CASCI computations. Our preliminary investigation considered the effect of the orbital and total angular momentum constraints on the reduced-density matrices (RDMs) of atomic systems. Multiple angular momentum states can be modeled by placing constraints on the expectation values of both the square of the orbital angular momentum operator and the z-projection of the orbital angular momentum operator. We have found that these constraints not only allow us to describe electronically excited states that are otherwise inaccessible, but they can improve the description of previously accessible ones.

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# Cluster perturbation theory for energies and molecular properties

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We introduce a new class of perturbation models—the cluster perturbation (CP) models—where the major drawbacks of Møller-Plesset and coupled cluster (CC) perturbation theories have been overcome. In CP theory, we consider a target excitation space relative to the Hartree-Fock state and partition this target excitation space into a parent and an auxiliary excitation space. The zeroth-order state is a CC state in the parent space and the target state is the CC state in the target space. Perturbation series, leading from the zeroth-order, parent state to the target state, is in CP theory determined in orders in the similarity-transformed fluctuation potential, where the similarity transformation is carried out using a cluster operator describing the parent space. Perturbation series are in CP theory determined not only for the ground-state energy, but also for molecular properties, including excitation energies and frequency-dependent response properties, with the zeroth-order contribution in the series being the energy or the molecular property for the CC parent state and with the series formally converging to the energy or the molecular property for the CC target state. The applicability of CP theory to both the energy and molecular properties and the numerical results for the ground-state energy and excitation energies demonstrate the superiority of CP theory compared to previous perturbation models. Low-order corrections in the CP perturbation series may be expected to become state-of-the-art electronic structure models for determination of energies and molecular properties of target-state quality for single-configuration dominated molecular systems.

[1] F. Pawłowski, J. Olsen and P. Jørgensen, *Cluster perturbation theory. I. Theoretical foundation for a coupled cluster target state and ground-state energies*, J. Chem. Phys. **150**, 134108 (2019). DOI: 10.1063/1.5004037

[2] F. Pawłowski, J. Olsen and P. Jørgensen, *Cluster perturbation theory. II. Excitation energies for a coupled cluster target state*, J. Chem. Phys. **150**, 134109 (2019). DOI: 10.1063/1.5053167

[3] P. Baudin, F. Pawłowski, D. Bykov, D. Liakh, K. Kristensen, J. Olsen and P. Jørgensen, *Cluster perturbation theory. III. Perturbation series for coupled cluster singles and doubles excitation energies*, J. Chem. Phys. **150**, 134110 (2019). DOI: 10.1063/1.5046935

[4] F. Pawłowski, J. Olsen and P. Jørgensen, *Cluster perturbation theory. IV. Convergence of cluster perturbation series for energies and molecular properties*, J. Chem. Phys. **150**, 134111 (2019). DOI: 10.1063/1.5053622

[5] F. Pawłowski, J. Olsen and P. Jørgensen, *Cluster perturbation theory. V. Theoretical foundation for cluster linear target states*, J. Chem. Phys. **150**, 134112 (2019). DOI: 10.1063/1.5053627

# Dangers of the SCF-level DBOC: NO and NO<sub>2</sub> as examples

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The diagonal Born-Oppenheimer correction (DBOC) [1, 2], which accounts for the finite mass of the nucleus, plays a small but vital role in high-accuracy model chemistries such as HEAT [3–5], W4 [6], and others. The considerable complexity and expense of obtaining this correction with a correlated theory, such as coupled cluster [7], has encouraged most authors to evaluate the DBOC with Hartree-Fock, where it is comparatively easily obtained from the CPHF solutions [8] as per Handy *et al.* [9]. However, as has been previously demonstrated for force constants [10, 11], these solutions are a poor treatment of what may be considered the ‘SCF excited states’, and CPHF poles, where the CPHF solutions approach a singularity, are frequent troublemakers in quantum chemical calculations of radicals.

That the seemingly innocuous SCF-level DBOC, which depends on the CPHF solutions, is susceptible to the same problems as force constants is apparently not fully appreciated. Here, the NO and NO<sub>2</sub> radicals are used as case studies of such pathologies in the DBOC. The NO radical serves as an example of artificial fluctuations of the DBOC as a consequence of UHF instabilities, where better behavior is obtained at the CCSD and CCSDT levels of theory. The NO<sub>2</sub> radical demonstrates a true divergence of the DBOC at the crossing point of the <sup>2</sup>A<sub>1</sub> and <sup>2</sup>B<sub>2</sub> electronic configurations, where the adiabatic representation of molecules breaks down and model chemistries built within the Born-Oppenheimer framework should be treated with great care. Using these two examples, diagnostic tools for potential DBOC breakdowns will be presented.

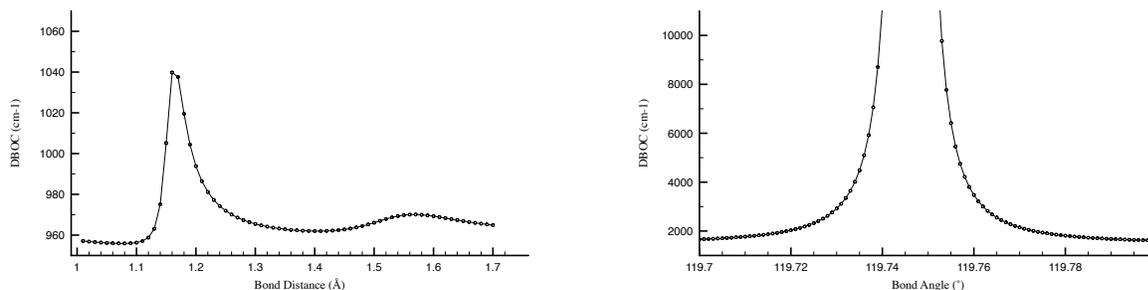


FIG. 1: Values of the DBOC (cm<sup>-1</sup>) as a function of bond length (Å) for NO (left) and bond angle (°) for NO<sub>2</sub> (right).

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# Practical Proxies of Couplings and Quantum Interferences among Pathways for Dexter Energy Transfer

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When global spin of a molecular assembly during energy transfer is conserved, but the spin of donor and acceptor is changed, the Förster mechanism is forbidden and the Dexter mechanism through exchange of electrons is dominant. Dexter energy transfer reaction includes singlet fission, triplet fusion and triplet energy transfer (TT), which are essential for light harvesting, energy conversion and other wide-ranging photoinduced phenomena. However, the molecular level understanding and calculation of Dexter energy transfer are still quite challenging.

We started with the study of the triplet fusion reaction during singlet oxygen photosensitization reaction, and built a kinetic model to calculate the reaction rates based on a divide-to-conquer principle.[1] Taking 6-aza-2-thiothymine as PS, the spatial factor of the reaction was investigated by calculating the rate along different directions and intermolecular distance.[2] Then we proposed proxies for estimating the coupling strength in both diabatic and adiabatic pictures for general Dexter energy transfer, and verified them with the reaction in Eq (1). The result explains the curiously small coupling to the  $1\Sigma_g$  state along specific incidence directions, and provides a comprehensive understanding of the reaction mechanism of Dexter energy transfer problems.[3]

Then we investigated the Dexter energy transfer in non-covalent assemblies with the pathway analysis based on quantum chemical calculation. We calculated the coupling strength of triplet energy transfer (TT) in various architectures: D–A, D–B–A, D–multi(B)–A and D-B-multi(A), using constrained DFT methods. The effective couplings of different pathways from 1-particle, 2-particle and through-space interactions were evaluated using configuration interaction with the constrained density functional theory (CDFT-CI) method, and quantum interference among them are interpreted. We found that 1-particle, 2-particle and through-space interactions all contribute significantly, generating many more pathways than for electron transfer.[4] The quantum interferences among them change dramatically with geometries, providing the possibility of control by molecular design.

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# On the Unification of Three Theories for the Kinetics of Crystal Nucleation

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Over the past fifty years a theory for crystal growth and nucleation, where a Fokker-Planck equation is coupled with a mass balance equation, has been used by several groups for the study of the kinetics of nucleation from the bulk solution. Another recent approach to the same problem defined a logistic differential equation which gave an expression for the number of critical nuclei formed as a function of time. Both of the theories lead to results for the kinetics of nucleation that agree with experimental reports. We show here that the two methods actually yield identical expressions for the nucleation rate. A third description is provided via the so called JMAK equation. We find that this famous formula, under certain conditions, predicts the same kinetic behavior as found using the other two methods. We then conjecture for there being a type of universality for the kinetics of crystal nucleation. Further, it is proposed that these models give a kinetic description for two-step and homogeneous nucleation. This result motivates a description of the induction period in terms of the behavior of the nucleation rate for nuclei generated by the two-step mechanism.

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## Improving Efficiency in Symmetry-Adapted Perturbation Theory via Empirical Dispersion

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From understanding reaction stereoselectivity in the catalysis of organic reactions to the increased {em in vivo} toxicity of chloro- versus methyl-substituted therapeutic agents for the prevention of stroke and other vascular diseases, symmetry adapted perturbation theory (SAPT) has become an indispensable computational tool offering physical insight into the fundamental nature of non-covalent interactions (NCI) in diverse chemical systems. Further application of SAPT to novel problems is limited primarily by its computational expense, which scales as the fifth power of system size [ $O(N^5)$ ] for even its most affordable variant, SAPT0. In order to reduce the expense of SAPT0 such that it may be applied more widely, we present here SAPT0-D, whereby the exact dispersion from SAPT0 has been replaced with an empirical dispersion correction inspired by the popular dispersion-corrected density functional theory (DFT-D3) family of methods. In this way, we simultaneously reduce the algorithmic scaling of SAPT0 from  $O(N^5)$   $\rightarrow$   $O(N^4)$  while retaining the physically meaningful interpretation of IE components characteristic of all SAPT methods. This order of magnitude reduction in scaling for SAPT0-D translates into a nearly 5x speedup over conventional SAPT0 when computing the interaction energy (IE) for a truncated subsystem of the HIV-II protease--indinavir complex with 195 atoms, while offering nearly equivalent accuracy to SAPT0 when compared against gold-standard reference IEs for a diverse set of nearly 5,000 bimolecular complexes. Thanks to its unique combination of accuracy, reduced expense, and physical insight, SAPT0-D can be reliably applied to interrogate NCI in large, chemically diverse systems which were previously inaccessible, thereby serving a vital role in the advancement of numerous fields in the computational molecular sciences.