

The lithium-thiophene riddle revisited

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Abstract:

A recent study of the interaction of a lithium atom with the thiophene molecule found a large disagreement between high-level coupled cluster (CCSD(T)/AVTZ) and quantum Monte Carlo (fixed-node diffusion Monte Carlo, or FNDMC) calculations. We address this ‘lithium-thiophene riddle’ by analyzing the influence of crucial FNDMC simulation parameters, namely the one-electron models, basis sets, and pseudopotentials used for the generation of the trial wave function. These are shown to have a significant impact on the calculated FNDMC interaction energies and good agreement between CCSD(T) and FNDMC is found when nodal hypersurfaces of sufficient quality are used. Based on our proposed consensus reference value, we go on to benchmark the standard toolbox of lower-level quantum chemistry methods for this model interaction. Newly-developed dispersion-corrected DFT methods perform reasonably well despite the partial charge transfer character of the interaction and might well be worthy of further study in larger lithium-thiophene systems.

1. Introduction

Conjugated organic polymers can combine semiconductor-like electronic properties with plastic-like mechanical properties. Both are easily tuneable by chemical modification. *Polythiophene* and its derivatives are especially interesting in the field of ‘plastic electronics’, and a recent theoretical study was devoted to the interaction between a lithium atom and the thiophene molecule

with lithium-thiophene used as a model building block for doped polythiophene polymers.¹ It was found that geometric parameters of lithium-thiophene can be described acceptably well even with mid-level computational approaches (MP2 with medium-sized basis sets). However, the accurate determination of the interaction energy requires high-level electron correlation methods, for which in addition significant basis set truncation effects were found.¹

These effects were then investigated in more detail in a second study, in which the lithium-thiophene charge-transfer-complex interaction energy was estimated using MP2, CCSD(T) and FNDMC methods.² The comparison of the two quantum-chemistry methods with FNDMC showed a considerable disagreement (-8.2 kcal/mol for CCSD(T)/AVTZ and +1.3(1.7) kcal/mol for FNDMC), which the authors were tempted to resolve in favor of quantum Monte Carlo. The authors argued, that FNDMC is completely free of one-electron and N -electron basis set truncation effects (which is true only in a technical sense because truncated trial wave functions are used) in contrast to CCSD(T) where they found rather a large basis set effect. The authors mention the fixed-node approximation as a possible source of error in FNDMC but believe the effect to be small due to the essentially mono-configurational nature of the lithium-thiophene wave function.² Unfortunately not much is known about the impact of the fixed-node error in molecular systems, particular when we inquire about the extent to which fixed-node errors cancel when looking at energy differences. The authors cite existing benchmark studies by Grossman³ and by Manten and Lüchow⁴ to support their view, stating that FNDMC calculations with Hartree-Fock trial wave functions give relative energies of a quality similar to CCSD(T) with large basis sets. This is true for the atomization energies of the first study. However this is not the case for the reaction energies of the second, where the FNDMC approach is only slightly better than CCSD(T)/cc-pVDZ - a level of theory not generally considered to give accurate thermochemistry⁵ - and it is much worse than CCSD(T)/cc-pVTZ. In this work we would like to address three questions left open by the previous studies: How sensitive are the FNDMC results towards the QMC simulation parameters (with one-electron models, basis sets and pseudopotentials being the most important ones)? Can we resolve the 'lithium-thiophene riddle', that is can we understand the origin of the unexpectedly large difference between the CCSD(T) and FNDMC approaches? Finally, what lower-level methods can be recommended as standard tools for the modeling of lithium-thiophene-type systems?

2. Methodological aspects

Coupled-cluster methods are commonly used in quantum chemistry, and quantum Monte Carlo is well established in condensed matter physics. In this section we thus consider only the key ideas important for understanding the present work, and the interested reader is referred to the cited publications for details beyond the following. In quantum chemistry Coulomb effects beyond the Hartree-Fock (HF) approximation in many-electron systems can be taken into account by expanding the wave function in a set of Slater determinants generated from the HF wave function by virtual excitations. The consideration of all possible determinants would allow an exact solution of the electronic Schrödinger equation for a given basis set, but the direct variational optimization of the determinant coefficients is manageable only for very small systems. This problem can be circumvented by constructing the determinants with excitations only up to a certain maximum order, which inevitably compromises the attainable accuracy. The accuracy also depends of course on the quality of the basis set in which the one-electron orbitals in the Slater matrices are expanded. Basis set convergence is usually slow for correlated methods, so that the inclusion of higher excitations and the use of larger basis sets have to be balanced.⁶ Reliable studies should therefore start with a systematic analysis of excitation-level and basis-set errors unless benchmark data for similar systems is available. A number of extensive benchmark studies in the past have contributed to establish the CCSD(T)/cc-pVXZ (X=3 or more) approach as the 'gold standard' in quantum chemistry.⁷ It has also become a standard technique to extrapolate the systematically converging basis set effects in so-called complete basis set (CBS) schemes. Here the effect of an incomplete basis in higher level methods like CCSD(T) can be deduced from calculations with basis sets of increasing size or from calculations at a lower level of theory (usually MP2).⁸

The major deficiency of all electronic structure theory methods that depend on the superposition of orbital configurations (including the coupled-cluster approach) is the absence of an explicit N -particle correlation of the electrons.⁶ The use of explicitly correlated wave functions, where the value of the many-electron wave function depends directly on the relative separation of pairs of particles and their position with respect to the nuclear framework, is quite possible in quantum

Monte Carlo (QMC), since the Monte Carlo integration method allows the efficient evaluation of the resulting multi-dimensional integrals.⁹ The most commonly used QMC method, FNDMC, is based on the mathematical equivalence of the imaginary-time Schrödinger equation with a generalized diffusion equation, so that electronic systems can be simulated via a combined diffusion and rate process. The correct Pauli antisymmetry for fermionic systems is enforced by using the nodal hypersurface of a trial wave function. The use of the exact nodal hypersurface would allow one to compute the exact ground state energy, but the use of approximate nodal hypersurfaces (e.g. from Hartree-Fock or density functional theory (DFT) calculations) leads to a so-called 'fixed node error' which is usually a very small percentage of the correlation energy.⁹ Fixed-node diffusion Monte Carlo (FNDMC) is widely used in theoretical physics for highly accurate computational electronic structure theory calculations.¹⁰ It has many very attractive features: it is a genuine many-body theory with an explicit description of electron correlation, it shows a favorable scaling of computational cost with system size (quadratic, at best), and involves a naturally parallel algorithm that can be made to scale almost linearly with the number of processors, allowing easy exploitation of grid resources as well as the new generation of 'petascale' machines.^{11,12} Because of these advantages, FNDMC has drawn attention also from quantum chemistry.^{3,4,11} Nevertheless, it cannot yet be considered as fully established in that field, mainly since there is relatively little systematic information regarding the effects of the (only) fundamental limitation of FNDMC - the fixed approximation mentioned above - in the calculation of molecular energies and energy differences. Our study aims to facilitate the wider use of the FNDMC method in chemistry by adding to the existing knowledge about the fixed-node approximation. More information about our FNDMC (and wave function theory) calculations can be found in the following section; the FNDMC method itself and the algorithms used are explained in detail elsewhere.¹³

3. Computational Details

We have used single-determinant HF and DFT trial wave functions of the Slater/Jastrow type¹⁴ for our QMC calculations. The Jastrow factor was composed of u (expansion order 4) and χ (expansion order 4) terms,¹⁵ using default non-linear parameters and cutoffs available in CASINO, while linear parameters were optimized by variance minimization. We have found such simple Jastrow

factors to be sufficient to exclude pseudopotential localization errors in a recent FNDMC study on molecular systems.¹⁶ All our QMC calculations are based on Burkatzki-Filippi-Dolg (BFD) pseudopotentials and corresponding Gaussian basis sets.¹⁷ The use of pseudopotentials in principle allows larger time steps but we have used small time steps of 0.002 a.u. in order to minimize the timestep error as much as possible. Time step extrapolation was not applied, because initial extrapolation tests using DFT-D geometries and PBE/BFD-VTZ trial wave functions showed no statistically significant effects on relative energies. Each FNDMC calculation consists of about 10^8 Monte Carlo steps distributed on several hundred processors with an ensemble target population of a hundred sampling configurations on each processor. Checks for equilibration length and population errors showed no effect on the presented relative energies. All QMC calculations were done with a specially adapted version of CASINO,¹³ via our two Volunteer Computing projects QMC@home and QuantumFIRE alpha (see below for details). PBE,¹⁸ TPSS,¹⁹ PBE0,²⁰ TPSSH and B3-LYP^{21,22} DFT calculations with dispersion corrections of DFT-D2²³ and DFT-D3²⁴ type were done using the Turbomole 5.9²⁵ software, QZVP Gaussian basis sets, and the RI approximation^{26,27} for two-electron integrals. HF, MP2 and CCSD(T) calculations were done with the MOLPRO²⁸ software using aug-cc-pVXZ (X=D,T,Q) and aug-cc-pCVTZ basis sets. AM1²⁹ and PM6³⁰ semiempirical QM calculations were done with the MOPAC2009³¹ program. Throughout our study, MP2/aug-cc-pVTZ geometries were used that are very close to the MP2/AVTZ geometries of the original study, which were found to agree well with experimental data.³² Tests with MP2/AVTZ and MP2/aug-cc-pVQZ geometries showed very small effects of 0.1 to 0.2 kcal/mol on the calculated interaction energies for both CCSD(T) and FNDMC.

Quantum Monte Carlo at home (QMC@home)³³ is a Volunteer Computing project, that allows volunteers from all over the world to donate spare computing time for scientific research in the area of quantum chemistry. Started as the first large-scale distributed computing project in *ab initio* electronic structure theory,¹¹ QMC@HOME uses the nearly ideal parallelizability of FNDMC to do massively-parallel FNDMC calculations on thousands of processors via the BOINC (Berkeley Open Infrastructure for Network Computing) Volunteer Computing platform.³⁴ Over the course of the last few years, QMC@home has continuously contributed tens of teraflops of computing power³⁵ which has contributed significantly to the wider use of QMC methods in chemistry.

The QuantumFIRE alpha Volunteer Computing project was designed to utilize the technical developments of QMC@home for the area of condensed matter physics and de Broglie-Bohm pilot wave theory.³⁶ During its alpha test phase in 2010, QuantumFIRE contributed several teraflops of computing power³⁵ to our FNDMC benchmark studies. The project is currently offline for the transition from alpha to beta test phase.

4. Results and Discussion

Before addressing the FNDMC part of the lithium-thiophene riddle we review the quantum chemistry results presented in reference.² Table 1 lists interaction energies for the lithium-thiophene systems from the original study (upper part) in comparison with results from this work (lower part). The original MP2 values seem to be converged within about 0.5-1.0 kcal/mol at AVTZ level (given the changes from AVTZ to AVQZ) to a value of about -4 kcal/mol. As the convergence behavior of MP2 and CCSD(T) is known to be very similar,⁶ the combination of the MP2 trend with the CCSD(T) data suggests an estimate of about -8 kcal/mol for the lithium-thiophene interaction energy. The authors of the original study also report counterpoise-corrected³⁷ data (0.1, -3.3 and -3.8 kcal/mol for MP2 with AVDZ, AVTZ and AVQZ basis sets as well as -4.4 and -7.5 kcal/mol for CCSD(T) with AVTZ and AVQZ) with very similar findings: an analogous basis set behavior for MP2 and CCSD(T), a very small basis set effect when going from from AVTZ to AVQZ, and a final estimate of about -8 kcal/mol (taking into account that the counterpoise correction usually 'overshoots' to some extent).

Additional MP2 and CCSD(T) values from this work in the lower part of the table show good agreement for HF and CCSD(T), but a considerable deviation for MP2 when compared to the data from the upper part. We were not able to reproduce the MP2 data from the original study. Possible reasons for this are effects from the non-standard AVXZ basis sets and probably different frozen-core settings. In good agreement with the original study, we find an interaction energy of -8.4 kcal/mol for our frozen-core CCSD(T)/aug-cc-pVTZ calculations. Our converged MP2 value is shifted to about -10 kcal/mol, which we believe to be very reasonable in comparison with the CCSD(T) data

Table 1. Comparison of wave-function theory results for the lithium-thiophene interaction energy. All values in kcal/mol.

method	type ^a	ΔE
HF/AVTZ ^b	FC	+11.3
MP2/AVDZ ^b	FC	-11.5
MP2/AVTZ ^b	FC	-4.2
MP2/AVQZ ^b	FC	-4.3
CCSD(T)/AVDZ ^b	FC	-6.4
CCSD(T)/AVTZ ^b	FC	-8.2
HF/aug-cc-pVTZ ^c	FC	+11.3
MP2/aug-cc-pVDZ ^c	FC	-7.3
MP2/aug-cc-pVTZ ^c	FC	-9.9
MP2/aug-cc-pVQZ ^c	FC	-10.0
MP2/aug-cc-pV(TQ)Z ^{cd}	FC	-10.2
CCSD(T)/aug-cc-pVDZ ^c	FC	-5.9
CCSD(T)/aug-cc-pVTZ ^c	FC	-8.4
CCSD(T)/aug-cc-pV(DT)Z ^{cd}	FC	-9.3
CCSD(T)/CBS ^{ce}	FC	-8.8
HF/aug-cc-pCVTZ ^c	AE	+11.5
MP2/aug-cc-pCVTZ ^c	AE	-11.2
CCSD(T)/aug-cc-pCVTZ ^c	AE	-9.5
core correction ^f		<-1.1
best estimate ^g	AE	-9 to -10

^a all-electron (AE) or frozen core (FC)

^b from reference,² AVTZ stands for a fully decontracted aug-cc-pVTZ basis

^c this work

^d aug-cc-pV(XY)Z corresponds to basis set extrapolation from XZ and YZ data points and aug-cc-pV(TQ)Z extrapolation for HF

^e CBS scheme corresponds to CCSD(T)/aug-cc-pVTZ + (MP2/aug-cc-pV(TQ)Z - MP2/aug-cc-pVTZ)

^f difference between frozen-core CCSD(T)/aug-cc-pVTZ and all electron CCSD(T)/aug-cc-pCVTZ

^g final all electron CCSD(T)/CBS estimate

for a partly dispersion-bound system (where MP2 should be lower than CCSD(T) because an unsaturated fragment is involved). The overall systematic behavior of our MP2 and CCSD(T) results gives further support to the correctness of this data.

The authors of the original study believed that the difference between the CCSD(T)/AVDZ and CCSD(T)/AVTZ results, in combination with the unsystematic basis set dependence of their MP2 results, show that calculations with larger basis sets are needed to apply extrapolation techniques.² We do not consider this view to be supported by the literature. Extrapolation techniques are found to be especially helpful when only double- and/or triple- ζ coupled-cluster data points (particularly in combination with triple- and quadruple- ζ MP2 data points) are available and a rather modest accuracy of around 2 kcal/mol is already very helpful.³⁸ Given the small change from MP2/aug-cc-pVTZ to MP2/aug-cc-pVQZ, no large change in the interaction energies should be expected. Table 1 shows that this is indeed the case for basis set extrapolation of the MP2 interaction energy (which gives -10.2 kcal/mol at the MP2/aug-cc-pV(TQ)Z level). This quantity is then used for the calculation of the CCSD(T) complete basis set (CBS) data (-8.8 kcal/mol for CCSD(T)/CBS, see reference⁸ for more information on the CBS scheme). The alternative scheme of extrapolating the CCSD(T) energies directly (instead of adding the MP2 basis set effect to CCSD(T) in the CBS approach) is likely to give a slightly less accurate estimate of the basis set dependence because only double- and/or triple- ζ data points are available. The agreement of the two extrapolation schemes within 0.5 kcal/mol (-8.8 kcal/mol for CCSD(T)/CBS and -9.3 kcal/mol for CCSD(T)/aug-cc-pV(DT)Z) is another indicator for the overall consistency of the wave-function theory data.

One factor not considered up to this point is the influence of core-correlation effects. This might be of importance because of the critical role of the lithium atom for which the frozen-core approximation could be expected to be less accurate. We therefore performed all-electron MP2 and CCSD(T) calculations with corresponding triple- ζ basis sets (aug-cc-pCVTZ) which can be compared to frozen-core calculations (with an aug-cc-pVTZ basis) in order to estimate the impact of core-correlation effects. The observed core effect of -1.1 kcal/mol includes to some extent basis set effects because of the necessary addition of special core functions and should therefore be

seen as an upper bound for the core correction.

Given the extensive literature on CCSD(T) calculations for molecular systems (see e.g. reference⁶ and references therein) and the fact that basis set extrapolation schemes have been shown to work reliably with rather high accuracy,³⁸ it seems very unlikely that our CCSD(T)-based best estimate of -9 to -10 kcal/mol (including core effects) should be off by more than 1-2 kcal/mol. Having established what seems to be a rather trustworthy value via the wave-function theory path, it now seems quite odd that the FNDMC approach of the original study gives a very different answer of $+1.3 \pm 1.7$ kcal/mol.

An obvious problem is of course the large statistical error, which does not allow a quantitative statement about the interaction energy of interest. Modern developments of computer technology and the almost ideal parallelizability of FNDMC open a route to do better here (see our earlier discussion of Volunteer Computing). FNDMC calculations can also profit from the use of pseudopotentials that increase the efficiency of the FNDMC sampling process, at the cost of a trade-off between additional pseudopotential errors and avoided core nodal errors. As for the error cancellation in standard quantum chemistry approaches the outcome of this trade-off is hard to judge from theoretical principles alone and – like the impact of the fixed node error itself – needs investigation in the form of benchmark studies.

In a recent study aiming in this direction,¹⁶ we were able to show that the basic trial wave function parameters like pseudopotentials, one-electron model, and basis set truncation can have a significant impact on energy differences. The combination of high-quality pseudopotentials, DFT determinants, and rather large one-electron basis sets allow accuracies comparable to CCSD(T)/cc-pVTZ in the calculation of energy differences in comparison with experimental reference values. With the results of this study in mind we have performed several FNDMC calculations with different trial wave functions for lithium-thiophene. Table 2 shows our results for the analysis of the influence of crucial FNDMC simulation parameters for this system.

In accordance with our earlier study we find a large effect stemming from the use of pseudopo-

Table 2. Comparison of pseudopotential (PP) and all-electron (AE) FNDMC results^a with wave function theory data for the lithium-thiophene interaction energy. All values in kcal/mol.

Method	ΔE
Pseudopotential influence	
AE-FNDMC(HF/AVTZ) ^b	1.3(17)
PP-FNDMC(HF/BFD-VTZ)	-7.0(1)
One electron model influence	
PP-FNDMC(PBE/BFD-VTZ)	-8.2(1)
DFT functional influence	
PP-FNDMC(B3-LYP/BFD-VTZ)	-8.3(1)
Basis set influence	
PP-FNDMC(PBE/BFD-VQZ)	-8.7(1)
Lithium PP influence	
PP/AE-FNDMC(PBE/BFD-VQZ) ^c	-8.3(1)
Wave function theory data	
CCSD(T)/AVTZ ^{bd}	-8.2
CCSD(T)/CBS ^d	-8.8
Best estimates	
wave function theory ^c	-9 to -10
quantum Monte Carlo	-8 to -9
consensus reference	-9 ± 1

^a XX-FNDMC(OEM/OEB) stands for all-electron (XX=AE) or pseudopotential (XX=PP) FNDMC calculations with trial wave functions based on the one electron model OEM (e.g. HF or a DFT functional) and the one electron basis OEB (e.g. BFD-VTZ, i.e.

Burkatzki-Filippi-Dolg triple- ζ basis sets)

^b From reference²

^c Lithium atom without PP

^d See table 1

tentials in the generation of the FNDMC trial wave function, again with substantial benefit from the trade-off between additional pseudopotential errors and avoided core nodal errors. (In contrast to our recent study we compare here to our wave-function theory best estimate and not experimental data, which is not available for this system.) Another gain in accuracy has its origin in the use of DFT trial wave functions, independent of the actual exchange-correlation functional used (again in accordance with our earlier study). The impact of large (quadruple- ζ) basis sets and the effect of also using a lithium pseudopotential is found to be smaller than the statistical error bars. From the above tests of the influence of basic trial wave function parameters on the interaction energy for the lithium-thiophene system we arrive at a FNDMC-based best estimate of about -8 to -9 kcal/mol (not taking core effects into account beyond the use of pseudopotentials).

Comparing our best estimates from wave function theory and quantum Monte Carlo, the ‘lithium-thiophene riddle’ seems to be solved: calculated FNDMC energy differences for the lithium-thiophene complex show significant sensitivity to the basic trial wave function parameters. This suggests that the essentially mono-configurational nature of the wave function of lithium-thiophene does not automatically guarantee a highly accurate description of its energetics with FNDMC. The implicit conclusion – that a mono-configurational character of the molecular wave function allows one to expect good cancellation of nodal (and other) errors – does at least not seem to hold for the calculation of relative energies with all-electron FNDMC and HF trial wave functions. CCSD(T)/CBS-level accuracy can nevertheless be achieved without going to multi-determinant trial wave functions (which do allow a systematic, but less practicable improvement) via the PP-FNDMC(DFT/BFD-VQZ) approach.

Combining our best estimates from wave function theory and quantum Monte Carlo one arrives at a consensus reference value of -9 ± 1 kcal/mol, according to a conservative error estimate. Based on this reference we will try to answer the question of which lower-level methods can be recommended as standard tools for the modeling of larger lithium-thiophene type systems. Table 3 shows DFT and semiempirical QM results for the lithium-thiophene interaction energy. This data can be used to support the following conclusions.

Table 3. Comparison of DFT and semiempirical QM results for the Lithium-thiophene interaction energy. All values in kcal/mol.

method	ΔE		
consensus reference ^a	-9 ± 1		
DFT methods ^b			
DFT functional	DFT	DFT-D3	DFT-D2
PBE	-10.2	-10.3	-15.0
TPSS	-10.1	-10.4	-16.6
PBE0	-9.9	-10.1	-13.8
TPSSH	-10.2	-10.5	-
B3-LYP	-7.6	-7.9	-14.3
Semiempirical QM methods			
PM6	-68.0		
AM1	+6.9		

^a see table 2

^b QZVP basis

All DFT functionals tested are doing acceptably well with deviations of about 1 to 1.5 kcal/mol. The effect of Fock-exchange mixing is found to be small for an (at least partial) CT-type interaction. The inclusion of dispersion effects via atom-pair wise corrections by the 'standard' DFT-D2 approach leads to strong over-binding, a problem which is well-known for many metal atoms. The improvements with the third-generation dispersion correction (DFT-D3) are substantial in comparison with DFT-D2. They have (as it should be), however, little impact on the 'pure' DFT values because metal-atom molecule dispersion is quenched at these short intermolecular distances which is correctly described by the D3-model. As dispersion interactions will become important for larger thiophene-lithium (or similar) systems, we would nevertheless recommend using DFT-D3 in general.

Semiempirical QM methods are often a valuable alternative to DFT methods, because they are two to three orders of magnitude faster and quite accurate for systems which are not too dissimilar to the ones used for the parametrization of the method. This is unfortunately not the case for lithium-thiophene, for which both PM6 and (to a lesser extend) AM1 are very inaccurate (other methods like OMx and SCC-DFTB do currently not have parameters for lithium available).

5. Conclusions

Returning to the three questions at the end of our introduction we are now able to give the following answers: the FNDMC results for lithium-thiophene show significant sensitivity with respect to basic trial wave function parameters. We find an especially large effect from pseudopotentials and a substantial benefit from the trade-off between additional pseudopotential errors and avoided core nodal errors when pseudopotentials are used. This is a very promising finding, because of the considerable advantages of FNDMC in exploiting modern computing architectures for the accurate computational treatment of larger molecular systems, where CCSD(T) quickly runs into both the 'scaling wall' and – nowadays even more important – the 'parallelizability wall'. Given the impact of basic trial wave function properties on the calculation of relative energies for molecular systems, we suggest to always check and include information about these trial wave function features when using FNDMC for chemistry. A good agreement between CCSD(T) and FNDMC is found at the PP-FNDMC(PBE/BFD-VQZ) level, which allowed us to establish a consensus reference value of -9 ± 1 kcal/mol for the lithium-thiophene interaction energy. From benchmarking the standard toolbox of lower-level quantum chemistry methods against this reference, D3-corrected PBE or TPSS based functionals emerge as possible candidate for the quantum-mechanical investigation of larger lithium-thiophene systems. Definitive statements about this would however require further studies along the entire interaction potential curve.

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