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Molecular Structure, Spectra, and Reactions The Development of New Theory, Its Implementation and Applications

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Molecular Structure and Spectra, the Development of New Theory its Implementations and Applications

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Abstract

In the last four years of our work for AFOSR, we have done a number of things that build on our proof of an exact, correlated orbital theory as an effective one-particle theory. The idea is to provide coupled-cluster (CC) accuracy for molecular structure and spectra, but within a computational framework that exploits its one-particle character. This makes it possible to do much larger systems than can be done in traditional CC theory, even with our development of massively parallel computer programs like ACES 3 and 4. This effort also ties to CC theory that has to converge to the correct answer in appropriate limits. COT has Kohn-Sham density functional theory (DFT) as a special case. Exploiting this connection has led to four new 'consistent' DFT functionals of the QTP family. Unlike conventional DFT[1], they provide an accurate one-particle spectrum, solve the problem of charge-transfer excited states in KS-DFT, provide accurate densities and activation barriers, give excellent fully relaxed core ionizations and excitation spectra, and ameliorate the pervasive self-interaction problem of KS-DFT. Several further developments are anticipated, including their extension to infinite polymers and solids.

I. Correlated Orbital Theory and Quantitative Molecular Orbital Theory

Our recent work for AFOSR has emphasized the concept of a 'Correlated Orbital Theory' (COT) meaning that we proved that there exists an effective one-particle Hamiltonian, such that its eigenvalues have to be the exact principal ionization potentials along with some exact electron affinities for unoccupied orbitals[2,3] (references are on pg. 17) The equation has the form,

(1)

where the critical quantity is the $\{\epsilon_p\}$. When the orbitals are occupied, *p= i, j, k, l* and unoccupied, *p=a, b, c, d*. This condition is analogous to Koopmans' approximation[4] in Hartree-Fock (HF) theory[5], but is now exact, $\epsilon_i = -I_i$ where I_i is the energy required to ionize the electron from the correlated orbital, i. For an electron affinity, $\epsilon_a = -EA_a$ where EA_a is the energy required to add an electron into orbital *a.* These can be both positive and negative depending upon whether the anion is bound. Most such EA values are negative (unbound) and lie in the continuum, so it is meaningless to speak of *all* unoccupied orbitals having eigenvalues that correspond to electron affinities.

The effective Hamiltonian in COT is shown[2] to be

(2)

where a one-particle correlation potential, $\Sigma_{CC}(1)$, has been added to the Fock operator, f. In the absence of $\Sigma_{CC}(1)$ one gets HF theory. In Kohn-Sham (KS) density functional theory(DFT) [6,7], one has this form where instead of the exchange operator and correlation potential, $-K + \Sigma_{CC}(1)$, one has V with the potential, V ——— of the KS energy funnctional. So both are special cases. In general, the COT operator is non-local in correlation and exchange. Originally, KS theory was formulated to only have a local, multiplicative V_{xc} but now the vast majority of approximations commonly use some percent of non-local HF exchange, K, like in the widely used B3LYP and most of the Minnesota and Berkeley functionals, etc. These methods are sometimes called 'generalized' Kohn-Sham[8].

In wavefunction theory, it has been known for some time that the Dyson equation[9] provides correlation corrections within a one-particle theory, but uses a frequency-dependent $h^{eff}(1, \omega)$,

(3)

where is the self-energy. To get its solutions, one has to solve ω-dependent equations

(4)

and one has a solution only when $\omega = \epsilon_p$ These solutions include all possible ionization and electron attached processes, like 'shake-ups' that involve additional electron re-arrangements as ionization occurs. Furthermore, these Dyson orbitals (amplitudes are better) are a non-orthogonal, over-determined set of solutions. They are useful for the evaluation of transition moments, but do not provide a MO theory of (bi)-orthogonal orbitals as in the COT Eqn. 1.

This is caused by the frequency dependence of the equation. To define the frequency independent COT equations we reconsidered the Dyson self-energy from the viewpoint of coupled-cluster theory[2]. This enabled us to focus on just the principal ionizations and attachments instead of all possibilities, and to replace the frequency dependent Dyson's self-energy by a frequency independent, $\Sigma_{CC}(1)$ that can be readily written down in terms of CC solutions.

If we view these new MO equations as the framework for a 'quantitative molecular orbital theory' of correlated orbitals, then several things should happen. First and foremost, each occupied orbital needs to be associated to its principal IP, and some of the unoccupied ones, particularly the LUMO, to an EA. This means that the 'Frontier MO Theory' that attempts to rationalize some reactions based on the HOMO and LUMO orbitals are now tied to observable quantities instead of some nebulous Hückel definition.

Another consequence of this condition is what we call the HOMO/LUMO condition. That is, the HOMO IP for F^- should have a HOMO eigenvalue equal to its IP, but the F atom's LUMO eigenvalue should be equal to its EA. Though certainly true thermodynamically, it is not typically true in theory, particularly in KS-DFT; especially with regard to the eigenvalues as opposed to energy functional differences. However, even in wavefunction theory, the differences in the results between treating open and closed shells would cause this condition to not be as well satisfied as it should be. It is very well known that the eigenvalues of the KS-DFT equations are far from the correct IP values, as shown in Figure 1.

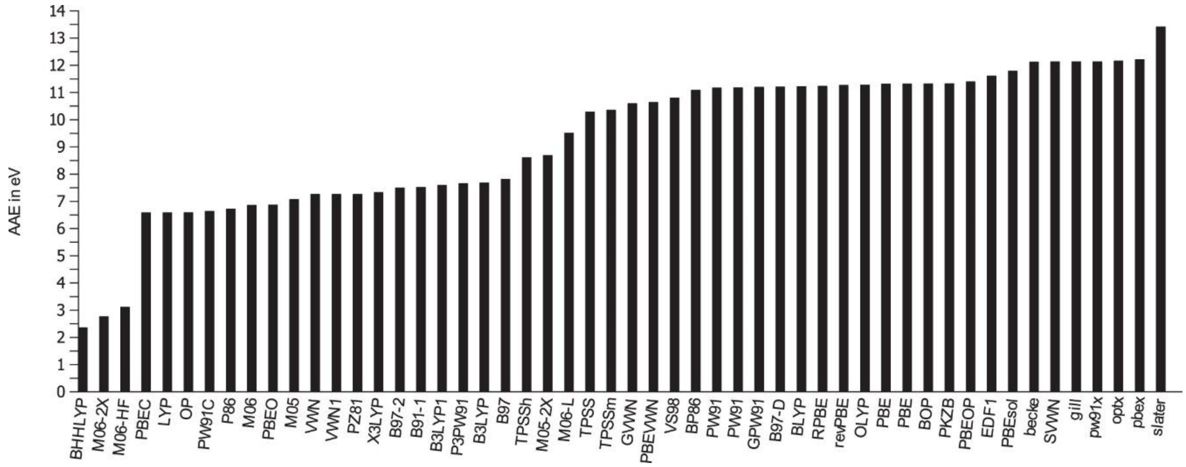


Figure 1. Performance of DFT potential for the characterization of the vertical ionization energies in eV as the negative of eigenvalues of the KS operator $((-\epsilon_i = I_i, i \in all\ occupied\ orbitals))$

In Figure 1 we are plotting the average absolute error for *all* the occupied orbital eigenvalues compared to exp. Ip's for the many functionals shown, which ranges from 2.5 eV to the 20's. But this failure even pertains for the HOMO orbital as shown in Figure 2, that in an exact DFT has to give the first IP,

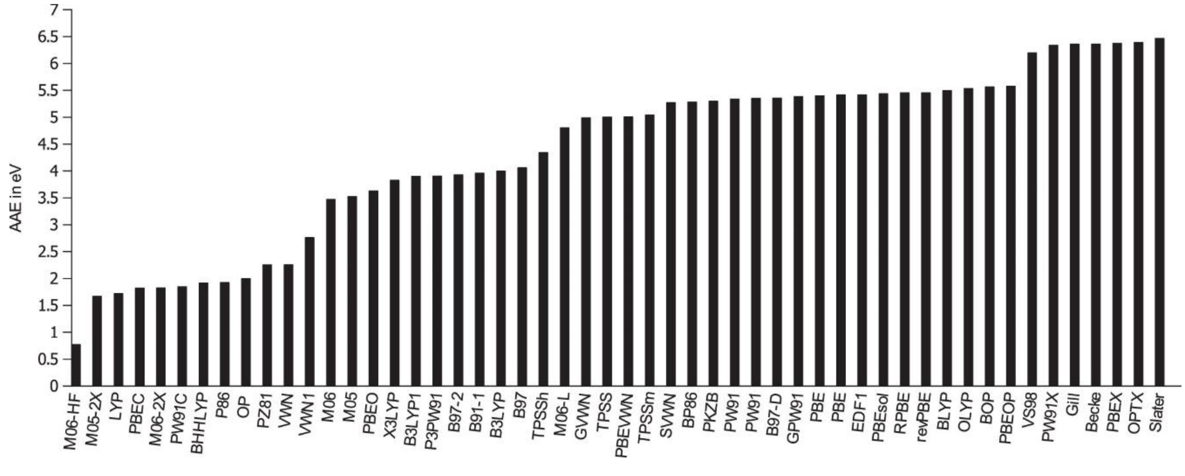


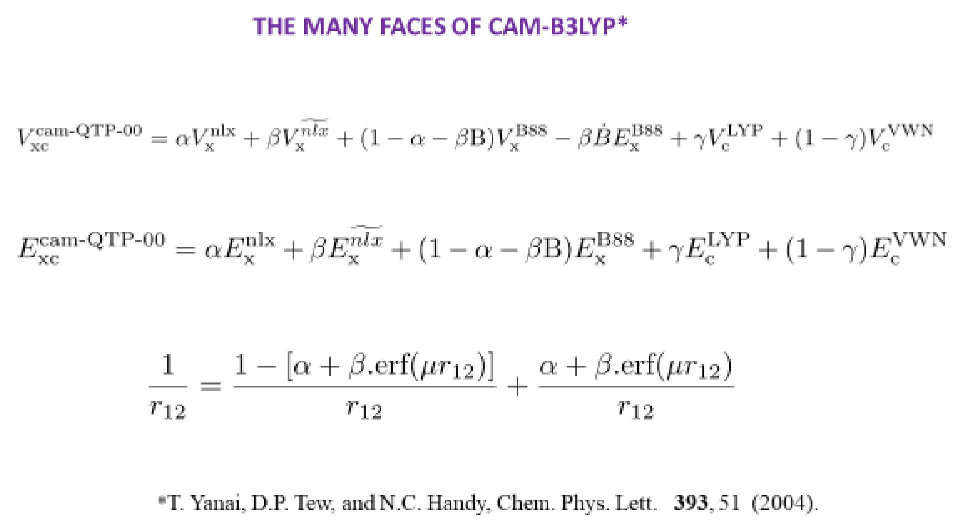
Figure 2. Performance of DFT potential for the characterization of the vertical ionization energies in eV as the negative of eigenvalues of the KS operator $((-\epsilon_i = I_i, i \in HOMO\ orbitals))$

So in practice, KS-DFT approximations are far from satisfying the condition that their eigenvalues provide decent approximations to all the principal IP's or even for the HOMO. However, this should not be the case, based upon an IP theorem we proved.

Adiabatic, time-dependent KS-DFT is meant to provide the excited state analogue to ground state KS-DFT using the same frequency independent form of functional as in the ground state. Consequently, if an electron is excited through a series of Rydberg states to its ionization continuum, the excitation energy should smoothly change into the ionization potential. This requires that the ground state KS eigenvalues are reasonable approximations to all the principal Ip's. This can be verified numerically with any Gaussian based TDDFT program by simply adding a very diffuse basis function into the basis set (exponent like 10^{-70}) This zero-differential overlap (ZDO) function has no overlap with any other function in the basis and has a zero orbital energy. Then it is easy to show that all the two-electron integrals and other terms in the TDDFT equations disappear, leaving *only the ground state orbital eigenvalues*. Hence, contrary to conventional KS-DFT wisdom that states that the KS orbitals have no meaning except to represent the density, their eigenvalues are given meaning via adiabatic TDDFT. This is our IP-eigenvalue theorem. Thus, this is a required condition in a 'consistent' KS-DFT approximation, and in our opinion, an important one.

To fix this, we introduced a new parameterization for KS-DFT functionals and potentials. We take standard KS-DFT approximations for the functional and its potential, and use the flexibility built into the form in terms of its parameters to ensure that we satisfy our IP conditions for all occupied orbitals up to a threshold. This will define the new QTP family of KS-DFT functionals that are minimally parameterized compared to the others being developed like those at Minnesota that can have as many as 263 parameters! This will also provide a framework for 'Quantitative MO Theory.'

A recent Frontier paper in CPL[3] discusses what we have accomplished to date. Using the well-known range-separated form of functional, CAM-B3LYP, Figure 3.



THE MANY FACES OF CAM-B3LYP*

$$V_{\mathrm{xc}}^{\text{cam-QTP-00}} = \alpha V_{\mathrm{x}}^{\mathrm{nlx}} + \beta V_{\mathrm{x}}^{\widetilde{nlx}} + (1-\alpha-\beta\mathrm{B})V_{\mathrm{x}}^{\mathrm{B88}} - \beta\dot{B}E_{\mathrm{x}}^{\mathrm{B88}} + \gamma V_{\mathrm{c}}^{\mathrm{LYP}} + (1-\gamma)V_{\mathrm{c}}^{\mathrm{VWN}}$$

$$E_{\mathrm{xc}}^{\text{cam-QTP-00}} = \alpha E_{\mathrm{x}}^{\mathrm{nlx}} + \beta E_{\mathrm{x}}^{\widetilde{nlx}} + (1-\alpha-\beta\mathrm{B})E_{\mathrm{x}}^{\mathrm{B88}} + \gamma E_{\mathrm{c}}^{\mathrm{LYP}} + (1-\gamma)E_{\mathrm{c}}^{\mathrm{VWN}}$$

$$\frac{1}{r_{12}} = \frac{1-[\alpha+\beta.\mathrm{erf}(\mu r_{12})]}{r_{12}} + \frac{\alpha+\beta.\mathrm{erf}(\mu r_{12})}{r_{12}}$$

*T. Yanai, D.P. Tew, and N.C. Handy, Chem. Phys. Lett. **393**, 51 (2004).

Figure 3. Potential and exchange functional form of CAM-B3LYP.

that has four parameters, α, β, γ and the range-separation parameter, μ we adjusted them in the CAM-B3LYP *potential,* V^{XC} only to represent the five IP's of the water molecule whose worst case was within about ~0.8 eV of experiment. No other molecule was considered and no other data used in the parameterization, since our objective was to test the role of our IP-eigenvalue theorem. This also means that $\epsilon_m = \langle m|h^{eff}|m\rangle = \langle m|h + J + K + V_{xc}|m\rangle$, and the degree to which $\epsilon_m \simeq -I_m$ dictates the accuracy. In particular, this condition on the potential reduces what would normally be a first-order error in V_{xc} in $\rho(1)$, because $E[\rho(1)]$, as a variational solution has to be correct to second order, so its functional derivative, $V_{XC,}$ is only correct to first order. We define such KS-DFT methods as 'consistent' since the energy functionals and the potential are both required to be accurate. The latter also ensures that the IP's properly correspond to those TDDFT excited states that correspond to ionizations. All other KS-DFT methods in use today are not 'consistent.'

The results obtained were rather remarkable. For all other molecules considered, the fit to water's IP spectrum sufficed to give the IP spectrum (i.e. the single particle spectrum) to within the same tolerance. This answers the question what if we had used a different molecule to set our parameters? It would not have mattered. Furthermore, we then computed all the activation barriers in the well-known data sets with our CAM-QTP(00) functional, and our answers were in error by only ~2-3 kcal/mol for all reactions. Finally, we used this method to study the problem of core ionization and excitation spectra getting results accurate to ~1 eV. Core-excitation spectra is one of the main current interests of AFOSR with several experimental groups doing NEXAFS, XPS, etc. and we wanted to offer coordinate theoretical approach.

Note that the core ionization is well known to suffer from the greatest amount of orbital relaxation when an electron is ionized from a 1s orbital, as the reduced screening due to that electron basically changes the Z value of the atom to Z+1. So although it is well known that this relaxed value can be computed from two completely relaxed Hartree-Fock SCF calculations via subtraction (correlation is not significant for the core difference), within a QTP(00) calculation of only the neutral, simply the orbital eigenvalue for the 1s electron provides the right answer to ~1eV. This is by far the easiest way to get such values for ESCA and XPS spectra at least for molecules composed of H, B, C, N, O, F, atoms. Since the relaxation is properly included, the subsequent core-excitation spectra from TDDFT is similarly accurate. With no changes in our 4 parameters, for second-row atoms, our results are in error by only 0.23 % which is ~5 eV because of the very large core ionization values[3]. Figure 5 shows the exceptional accuracy of QTP(00) and QTP(17)*, for core ionizations. QTP(17) is also a global hybrid, so our results are not limited to range-separated forms, but should have a wide role in the field regardless of what parameterized KS form is used. Limiting those to 'consistent' forms should pay substantial benefits.

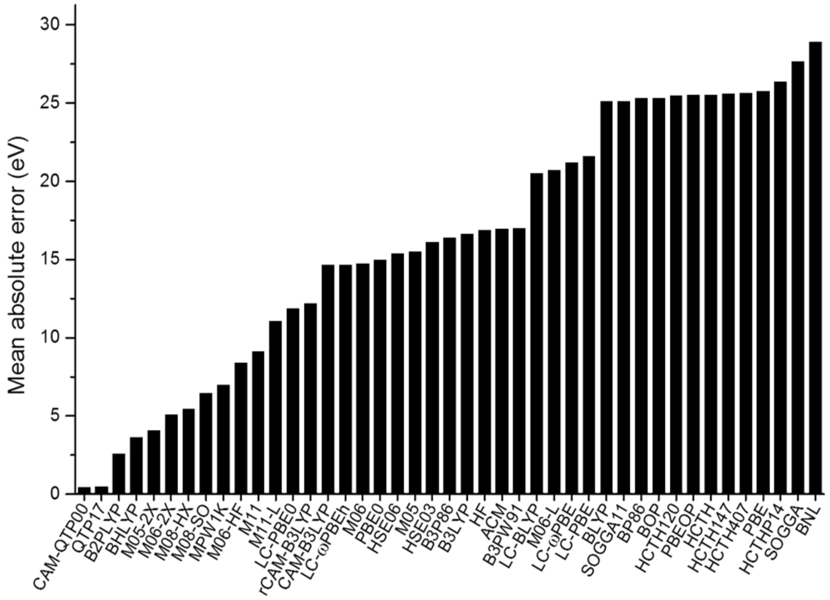


Figure 4. The mean absolute errors of core-ionization energies of some selected density functionals.

Adding to CAM-QTP(00) are (01) and (02). The first sacrifices the core ionization of water, keeping only the four valence IP's and adds in some additional information about Rydberg excitations. The results for the 'valence' only IP's are shown in **Figure 5.**

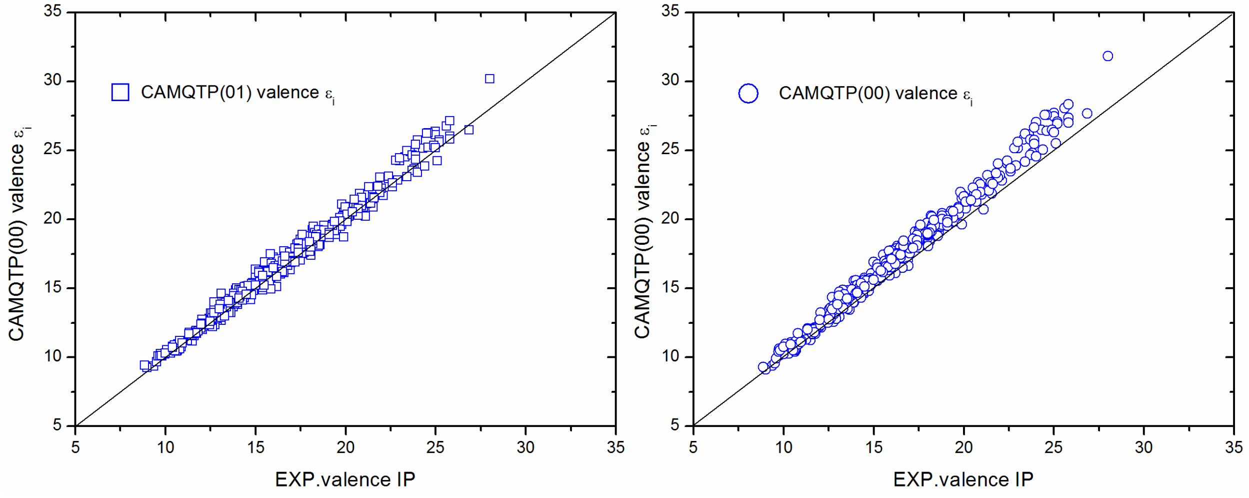


Figure 5. The mean absolute errors of 402 valence-ionization energies taken form 63 molecules for CAM-QTP00 and CAMQTP01 density functional eigenvalues. Units are in eV.

It's clear the results are a bit better for higher values of the 'valence' ionizations in (01) (not the core), as are a number of other properties, summarized elsewhere[10]. In particular, for excited states, the results of TDDFT QTP(01) are competitive with EOM-CCSD at a MAD of ~0.29 eV, that is better than QTP (00). But by excluding the core IP of water in its one-molecule IP parameterization, interestingly, QTP(01) does not correctly describe core ionizations and excitations.

The most recent functional CAM-QTP(02)[11], exploits the HOMO-LUMO condition to fix its three parameters, α, β and μ, γ is eliminated by restricting the correlation potential to just LYP instead of a γ

weighted combination of LYP and LDA's SVWN. The only condition we require is that the HOMO-LUMO condition for water and for the OH radical be satisfied. That is, we want water's HOMO IP to equal the water cations' LUMO EA, and for the OH^- IP to be the EA of OH neutral. Both conditions can be satisfied to ~0.75 eV. This is the degree to which the well-known discontinuity in V_{xc}[12] differs from the straight-line that should connect changes in electron number. The fourth-method eliminates α to give a long-range corrected form, LC-QTP to assess what effect that effect, alone, has.

When all are compared, we see the results summarized below:

Table I. Vertical ionization potentials from negative of occupied orbital eigenvalues for QTP family

	CAM-QTP-00[a]	**CAM-QTP-01[a]**	**CAM-QTP-02**	**LC-QTP**
MAD (all)	**0.93**	**0.41**	**0.56**	**0.71**
MAD (HOMO)	**0.32**	**0.24**	**0.23**	**0.39**

[a] From J. Chem. Phys. 145, 034107 (2016).
Mean absolute deviation (MAD) values in eV.

*Table II. Vertical excitation energies of 30 valence states and 39 Rydberg states. Geometries and reference values are taken from ref[13]. All the calculations use 6-311(3+,3+)G** basis sets.*

	CAM-QTP-00[a]	**CAM-QTP-01[a]**	**CAM-QTP-02**	**LC-QTP**	**EOM-CCSD[b]**
MAD (all)	**0.60**	**0.29**	**0.36**	**0.45**	**0.27**
MAD (valence)	**0.71**	**0.46**	**0.49**	**0.48**	**0.47**
MAD (Rydberg)	**0.52**	**0.17**	**0.26**	**0.42**	**0.11**

[a] From J. Chem. Phys. 145, 034107 (2016).
[b] From J. Chem.Theory Comput. 6, 370 (2010).
Mean absolute deviation (MAD) values in eV.

Table III. Hydrogen transfer (HT) and non-hydrogen transfer(NHT) reaction barrier heights. Geometries are optimized using aug-cc-pvtz basis sets. Reference values are taken from ref[14].

HT set	**CAM-B3LYP[a]**	**CAM-QTP-00[a]**	**CAM-QTP-01[a]**	**CAM-QTP-02**	**LC-QTP**
MAD	**2.8**	**2.3**	**2.7**	**2.2**	**1.8**
MAX	**6.1**	**6.2**	**5.0**	**4.6**	**5.0**

[a] Results provided by the authors of J. Chem. Phys. 145, 034107 (2016).
36 barrier heights with reference values from J. Phys. Chem. A 106, 842 (2002).

NHT set	**CAM-B3LYP[a]**	**CAM-QTP-00[a]**	**CAM-QTP-01[a]**	**CAM-QTP-02**	**LC-QTP**
MAD	**2.38**	**3.02**	**2.22**	**2.15**	**2.54**
MAX	**8.99**	**12.56**	**7.50**	**6.29**	**5.99**

[a] Results provided by the authors of J. Chem. Phys. 145, 034107 (2016).
38 barrier heights with reference values from J. Phys. Chem. A 109, 2012 (2005).
All data in kcal/mol.

In a quantitative MO theory, the LUMO has a critical role. Its eigenvalue should correspond to the molecule's electron affinity, whether bound or not. Nothing in QTP(00) or QTP(01) uses any information about the LUMO's EA, only that if we fix the IP's, then it ought to also follow that we know the IP's for F^- and F, which ties the IP to the EA, and makes the EA a by-product of our IP theorem. Instead, in QTP(02) this HOMO/LUMO property is solely used to define the method from water and hydroxyl. Nevertheless, notice the quality of the results obtained for EA's compared to experiment and the very high-level, ΔCCSDT-3 differences, ΔE(02).

Table IV. Electron affinities from CCSDT-3 and various KS-DFT methods.

	CAM-B3LYP	CAM-QTP00	CAM-QTP01	CAM-QTP02	LC-QTP	ΔE(02)	ΔE(Ref)
LiH	0.759	0.462	0.395	0.368	0.355	0.308	0.294
CH	2.551	1.115	1.425	1.153	1.064	1.232	1.168
NH	1.692	0.137	0.546	0.266	0.260	0.284	0.297
NH_3	-0.113	-0.436	-0.487	-0.522	-0.543	-0.581	-0.550
OH	3.281	1.132	1.974	1.565	1.725	1.660	1.802
H_2O	-0.014	-0.394	-0.437	-0.477	-0.494	-0.552	-0.556
HF	0.004	-0.406	-0.440	-0.481	-0.491	-0.570	-0.621
LiF	0.801	0.509	0.455	0.435	0.424	0.365	0.333
CN	5.472	4.140	4.383	4.132	4.041	4.220	3.834
HCN	-0.188	-0.390	-0.444	-0.461	-0.469	-0.477	-0.480
CO	-1.004	-1.306	-1.371	-1.402	-1.418	-1.391	-1.438
H_2CO	-0.206	-0.444	-0.502	-0.524	-0.532	-0.558	-0.543
CH_3OH	-0.164	-0.448	-0.495	-0.523	-0.535	-0.565	-0.535
H_2NNH_2	-0.116	-0.436	-0.486	-0.522	-0.543	-0.568	-0.505
NO	1.398	-0.280	0.137	-0.182	-0.219	-0.273	-0.465
O_2H_2	-0.112	-0.475	-0.517	-0.555	-0.571	-0.623	-0.620
H2	-0.880	-1.115	-1.153	-1.175	-1.181	-1.215	-1.231
Li_2	0.665	0.293	0.188	0.136	0.119	0.237	0.336
N_2	-1.494	-1.730	-1.788	-1.812	-1.822	-1.862	-1.829
O_2	1.642	-0.294	0.309	-0.071	0.004	-0.177	-0.129
F_2	2.260	-0.400	0.680	0.171	0.419	-0.099	0.392
MAD	0.823	0.193	0.177	0.096	0.076	0.085	
MAX	1.868	0.792	0.602	0.298	0.246	0.491	

All data in eV.

Note that the EA's are both positive and negative as they should be. The MAD for QTP(02) being less than 0.1eV is rather amazing for such a simple calculation, an accuracy competitive with high-level CC. The older two QTP functionals are still quite good, with about twice the error of QTP(02), while CAM-B3LYP shows how poor conventional methods are.

One outstanding problem for KS-DFT and its TDDFT generalizations has been the correct treatment of charge-transfer excited states. A wavefunction method that does this right is our similarity-transformed equation of motion (STEOM) approach[15,16], since it can smoothly go to $A^{+} + \mathrm{B}^{-}$ while even EOM-CCSD cannot do that exactly. For the model system of fluoroethylene versus ethylene, Figure 6 shows the results as a function of the distance between the molecules.

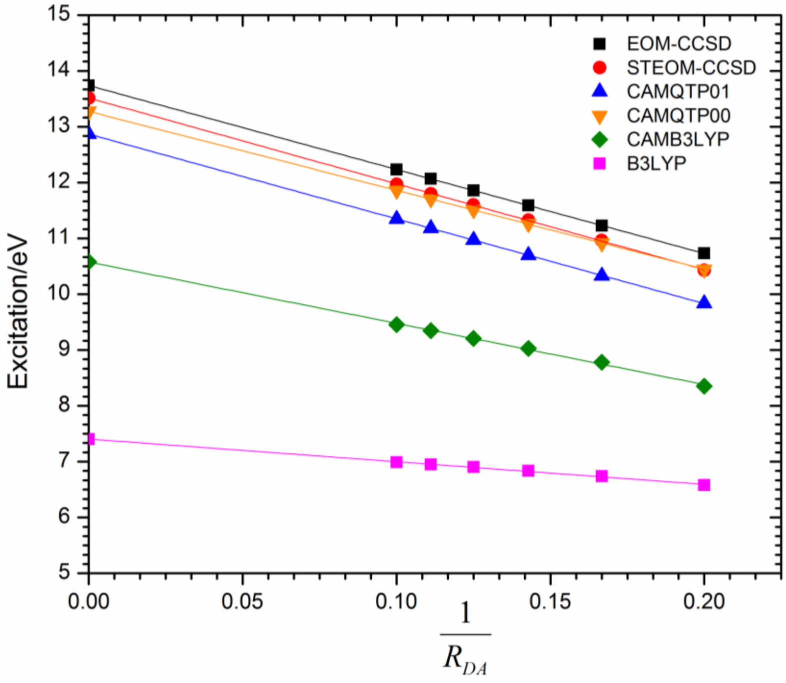


Figure 6.Charge transfer excitation between ethylene and fluoroethylene. Calculations use cc-pvtz basis sets.

Only the QTP functionals show good agreement, with QTP(00) being nearly on top of the STEOM results, unlike B3LYP and CAM-B3LYP. This CT condition is one that a quantitative MO theory should satisfy, and by virtue of our IP theorem and its associated effects on the EA, our 'consistent' QTP functionals can make a case for being a framework for a quantitative MO theory (QMOT).

Figure 7 shows how well QTP(02) does.

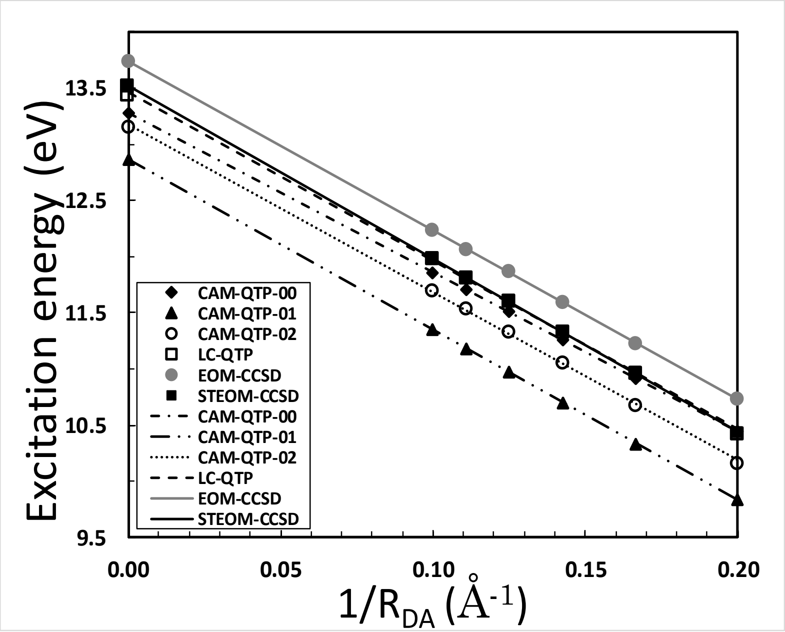


Figure 7. Charge transfer excitation between ethylene and fluoroethylene. Calculations use cc-pvtz basis sets.

Some other charge-transfer examples are seen in Table V.

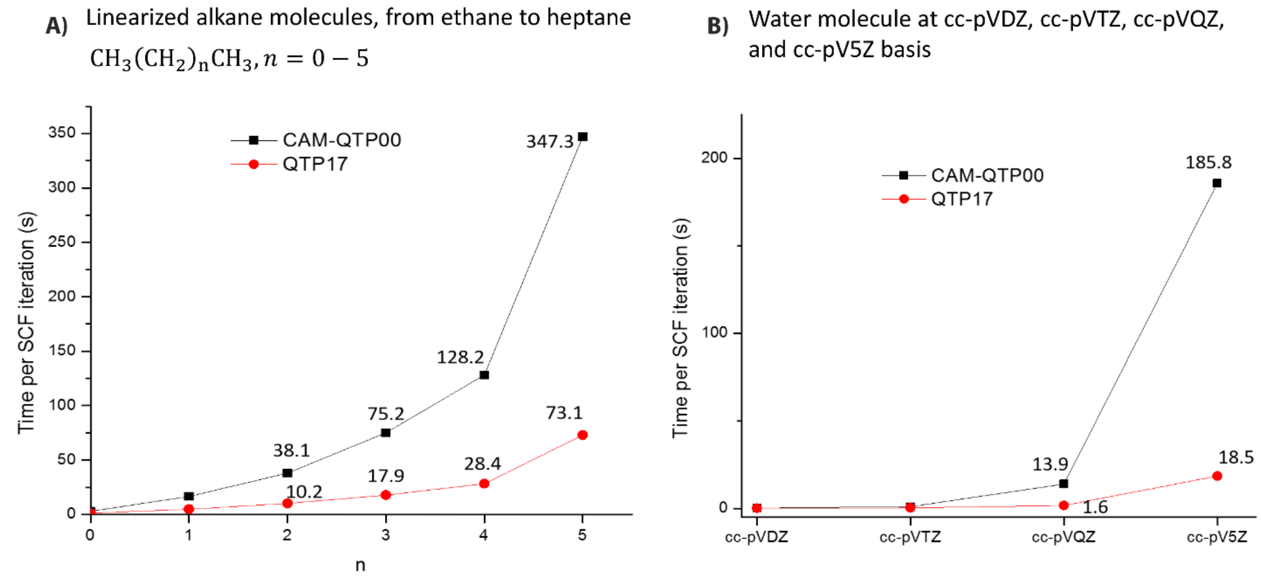
Table V. Charge transfer excitations in aromatic(Ar)…tetracyanoethylene complexes with fixed interplanar distances. Reference values and geometries were taken from ref[17]. Calculations use cc-pvtz basis sets.

Ar	CAM-QTP-00	CAM-QTP-01	CAM-QTP-02	LC-QTP	Exp[a]
Benzene	3.79	3.69	3.85	4.08	3.59
Toluene	3.46	3.35	3.50	3.73	3.36
o-xylene	3.21	3.10	3.25	3.47	3.15
Naphtalene	2.71	2.65	2.80	3.03	2.60
	3.48	3.42	3.57	3.79	3.23
MAD	0.14	0.08	0.21	0.44	
MAX	0.25	0.19	0.34	0.56	

[a] From J. Chem. Phys. 140, 18A502 (2014).

All data in eV.

Future Directions: As is apparent from the above summary of our work in this area, we have had a number of major successes during this funding period, but there are several new items to study in the next funding period.. One is to apply our IP-eigenvalue theorem to other algebraic forms of functionals and potetials. To illustrate, the functional QTP(17)[18] is solely directed at core ionizations and excitations, but it has a great computational advantage over the range-separated versions, shown in Figure 8.



A) Linearized alkane molecules, from ethane to heptane $\mathrm{CH_3(CH_2)_nCH_3}, n = 0 - 5$

B) Water molecule at cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z basis

Figure 8. Computational cost comparison between CAM-QTP00 and QTP17. Figure 8(A) shows the scaling of cost relative to size of the system. Figure 8(B) shows scaling of the cost relative to size of the basis set.

This attests to the fact that our theorem may be applied to virtually any form of density functional to improve its performance, not just range-separated ones. In fact, we plan to create some new onses.

Another route we want to pursue is the further development of the fully *ab initio* 'correlation' potential defined by COT. The numerical results obtained from it have to be equivalent to those from IP/EA-EOM-CC, but the rigorous first -principle one-electron correlation potential that COT shows exists, has not been adequately studied itself. The closest analogue would be the correlated optimized-effective potentials we obtained in our *ab initio DFT* work of a few years ago[19]. But as in all OEP work, such a potential is multiplicative, rather than non-local as would be the one derived in COT. That has the advantage that it can be plotted, but has the disadvantage that it is not the most general correlation potential possible. The very issue of 'local' vs. 'non-local' has not be addressed thoroughly. In COT we are talking about inverting the CC treatment of electron correlation to operate as an effective, non-local one-particle theory instead of a way to produce very accurate wavefunctions. I argue that that should be part of the unified treatment of electronic structure to embrace all approaches from Dyson to Kohn-Sham to naïve MO theory.

The next logical development should be to apply our QTP functionals to the band theory of solids. Figures 9 and 10 shows what happens when IP-EOM-CCSD and EA-EOM-CCSD are applied to increasing sizes of clusters. Only the QTP functionals QTP(00) and (01) exactly follow the EOM-CC results. The next step is to take such problems to the infinite cluster limit. That’s the main topic of solid-state physics. The fact that for finite systems the homo-lumo gap is right, implies that this feature will be pertinent to the band gap of solids. This is one place where the one-particle nature of COT as manifested into KS-DFT is immediately applicable, as there is no problem with imposing periodic boundary conditions on one-particle methods, but substantial ones for CC, eg. However, one has to be careful that the QTP functionals have the feature that they become 100% Hartree-Fock exchange in the long range limit of the range separation, which might be undesirable for infinite periodic systems, unlike molecules.

Fig. 9

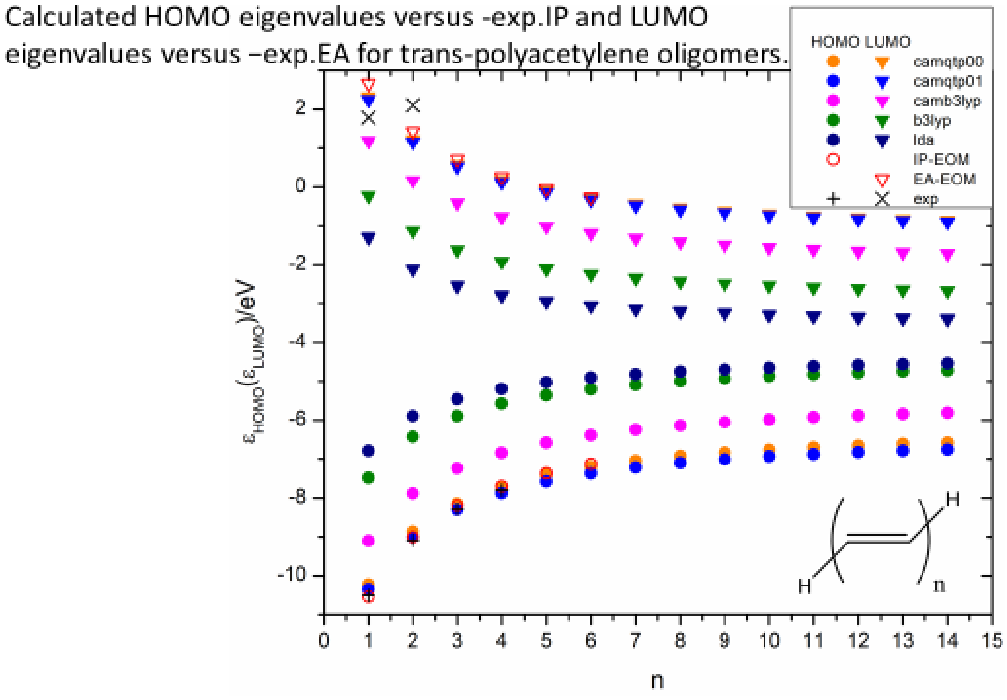
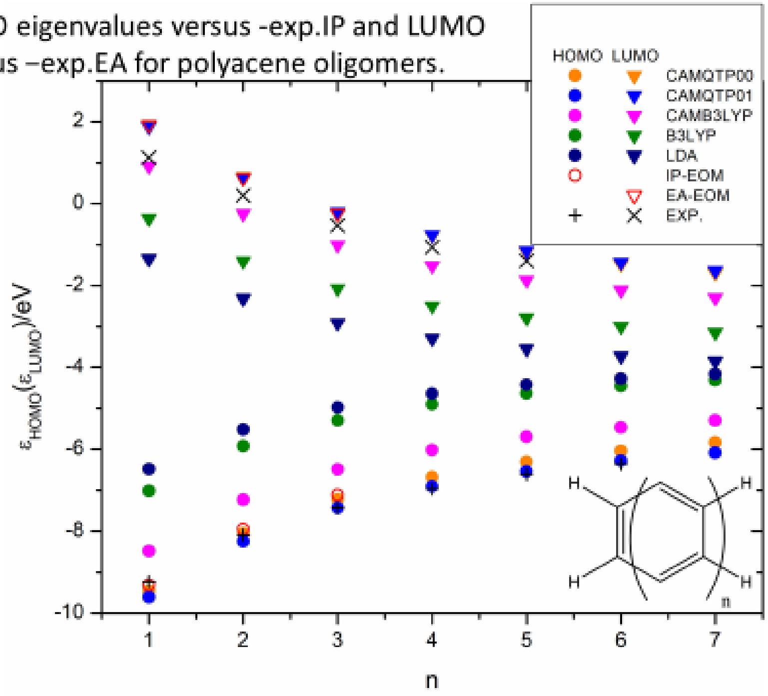

Calculated HOMO eigenvalues versus -exp.IP and LUMO eigenvalues versus −exp.EA for trans-polyacetylene oligomers.

Fig. 10

Calculated HOMO eigenvalues versus -exp.IP and LUMO eigenvalues versus −exp.EA for polyacene oligomers.



The further developments of QMOT have to include valence excitation energies obtained from simple expressions that will likely depend upon orbital energies for cations, not neutrals, as the latter have been shown to correspond to IP's and EA's. Combinations of those are well-known to not provide accurate results except for CT. For other kinds of valence and Rydberg excited states other expressions, should pertain, and so-far it appears the simplest will be tied to cation orbital energies. (haiduke, Bartlett, J. Chem. Phys., in press, see below)

Qualitative MO theory provides much of our conceptual understanding of chemistry. COT tells us that there is a quantitative generalization in that the occupied MO's should correspond to principal IPs and some unoccupied ones to EA's. So now, in addition to the usual symmetry, bonding and anti-bonding, properties of qualitative MO's. one can add how these orbital energies change with geometry, in reactions, or with occupation. But to describe some properties normally associated with total energies in terms of orbital energies, requires some procedure to exploit the latter information. Excitation energies are one such property that we show in this paper can often be obtained to good accuracy from the orbital energies. Total energies are another target.

Table I: Experimental data for vertical excitation energies and the respective values obtained with different theoretical approaches by means of calculations done with the aug-cc-pVTZ-mod basis set at the experimental geometry of each neutral system (in eV).[a]

Molecule	State	Eq. (4)[b]	Eq. (5)[b]	EE-EOM-CCSD	EE-EOM-CCSD(T)	Exp[c]
BeH ($^2\Sigma^+$)	$^2\pi$	2.57	2.51	2.52	2.51	2.48
	$^2\pi$	6.34	6.29	6.33	6.32	6.32
BeF ($^2\Sigma^+$)	$^2\pi$	4.23	4.18	4.18	4.16	4.14
	$^2\Sigma^+$	6.23	6.17	6.21	6.17	6.16
	$^2\Sigma^+$	6.31	6.25	6.29	6.26	6.27

CO ($^1\Sigma^+$)	$^3\pi$	6.54	6.40	6.40	6.39	6.32
	$^3\Sigma^+$	10.53	10.40	10.54	10.43	10.40
	$^3\Sigma^+$	11.41	11.28	11.42	11.30	11.30
	$^3\pi$	11.60	11.47	11.58	11.46	11.55
N_2 ($^1\Sigma_g^+$)	$^3\pi_g$	8.19	8.14	8.13	8.15	8.04
	$^3\Sigma_g^+$	11.96	11.90	11.95	11.94	12.00
H_2CO ($^1A_1$)	$^3A_2$	3.52	3.35	3.57	3.55	3.50
	$^3B_2$	7.02	6.85	7.03	6.98	6.83
	$^3A_1$	8.04	7.87	8.04	8.01	7.79
	$^3B_2$	7.84	7.67	7.85	7.82	7.96
H_2O ($^1A_1$)	$^3B_1$	7.20	7.26	7.21	7.25	7.0
	$^3A_2$	9.17	9.23	9.19	9.22	8.9
	$^3A_1$	9.78	9.84	9.78	9.82	9.81
	$^3B_1$	9.94	10.01	9.95	9.99	9.98
CH ($^2\pi$)	$^2\Sigma^+$	6.51	6.44	6.51	6.48	
	$^2\pi$	8.09	8.01	8.08	8.05	
	$^2\Sigma^+$	8.05	7.97	8.04	8.02	
	$^2\Sigma^+$	8.77	8.69	8.75	8.72	
	$^2\pi$	9.22	9.15	9.23	9.08	
	$^2\Sigma^+$	9.07	9.00	9.08	9.05	
CH_3 ($^2A''_2$)	$^2A'_1$	5.87	5.87	5.87	5.86	5.73
	$^2A''_2$	7.36	7.36	7.36	7.36	7.44
NO ($^2\pi$)	$^2\Sigma^+$	5.86	5.85	5.88	5.87	5.92
	$^2\pi$	6.92	6.91	6.87	6.87	6.9
	$^2\Sigma^+$	6.93	6.92	6.95	6.94	7.03
	$^2\Sigma^+$	7.98	7.97	7.99	7.98	
	$^2\pi$	8.23	8.22	8.23	8.22	
	$^2\Sigma^+$	8.39	8.38	8.39	8.39	
C_2H_4 (^1A_g)	$^3B_{1u}$	4.62	4.54	4.51	4.50	4.36
	$^3B_{3u}$	7.30	7.21	7.30	7.26	6.98
	$^3B_{1g}$	8.03	7.94	8.02	7.98	7.79
	^3A_g	8.31	8.22	8.31	8.28	8.15
	$^3B_{3u}$	8.87	8.79	8.88	8.84	8.57
MAD[d]		0.02	0.06	0.12	0.10	
MAX[d]		0.13	0.23	0.32	0.32	

[a] Core electrons are not included into the active space. Moreover, the open-shell systems are treated starting from a restricted open-shell Hartree-Fock reference;

[b] From IP-EOM-CCSD and EA-EOM-CCSD calculations;

[c] From Refs. [20–24];

[d] The mean absolute deviation (MAD) and maximum absolute deviation (MAX) values for EE-EOM-CCSD and EE-EOM-CCSD(T) are obtained with respect to experimental data. MADs and MAXs for eqs. (4) and (5) are calculated with respect to EE-EOM-CCSD results.

Next, we investigate the performance of some KS-DFT methods

Table II: Excitation energies obtained with the TD-DFT approach by means of calculations done with the aug-cc-pVTZ-mod basis set (in eV).[a]

Molecule	State	CAM-B3LYP	CAM-QTP-00	CAM-QTP-01	CAM-QTP-02	LC-QTP
BeH ($^2\Sigma^+$)	$^2\pi$	2.52	2.56	2.49	2.49	2.49
	$^2\pi$	6.08	6.37	6.06	6.09	6.27
BeF ($^2\Sigma^+$)	$^2\pi$	4.13	4.17	4.14	4.15	4.15
	$^2\Sigma^+$	5.85	6.14	5.98	6.02	6.15
	$^2\Sigma^+$	5.96	6.23	6.12	6.14	6.29
CO ($^1\Sigma^+$)	$^3\pi$	5.96	6.04	6.03	6.02	6.04
	$^3\Sigma^+$	9.92	10.71	10.19	10.32	10.51
	$^3\Sigma^+$	10.74	11.72	11.10	11.27	11.45
	$^3\pi$	10.83	11.89	11.23	11.40	11.61
N_2 ($^1\Sigma_g^+$)	$^3\pi_g$	7.86	8.18	8.02	8.07	8.14
	$^3\Sigma_g^+$	11.44	12.57	11.76	11.96	12.10
H_2CO ($^1A_1$)	$^3A_2$	3.25	3.46	3.27	3.29	3.27
	$^3B_2$	6.71	7.60	6.98	7.11	7.19
	$^3A_1$	7.64	8.62	7.95	8.10	8.17
	$^3B_2$	7.49	8.37	7.74	7.88	7.96
H_2O ($^1A_1$)	$^3B_1$	6.71	7.51	6.88	7.01	7.09
	$^3A_2$	8.54	9.47	8.80	8.96	9.08
	$^3A_1$	9.12	10.15	9.40	9.59	9.74
	$^3B_1$	9.22	10.34	9.51	9.71	9.86
CH ($^2\pi$)	$^2\Sigma^+$	6.15	6.80	6.35	6.48	6.66
	$^2\pi$	7.51	8.32	7.82	7.97	8.19
	$^2\Sigma^+$	7.57	8.27	7.76	7.90	8.13
	$^2\Sigma^+$	7.96	8.98	8.49	8.64	8.86
	$^2\pi$	8.67	9.50	8.93	9.09	9.32
	$^2\Sigma^+$	8.53	9.35	8.79	8.95	9.19
CH_3 ($^2A''_2$)	$^2A'_1$	5.51	6.04	5.70	5.80	6.03
	$^2A''_2$	7.00	7.61	7.18	7.30	7.55
NO ($^2\pi$)	$^2\Sigma^+$	5.43	6.38	5.65	5.82	5.90
	$^2\pi$	6.39	7.46	6.65	6.83	6.94
	$^2\Sigma^+$	6.39	7.48	6.69	6.89	7.00
	$^2\Sigma^+$	7.49	8.56	7.70	7.91	8.03
	$^2\pi$	8.09	9.07	7.94	8.16	8.31
	$^2\Sigma^+$	8.20	9.10	8.11	8.32	8.47
C_2H_4 (^1A_g)	$^3B_{1u}$	4.08	3.70	4.04	3.96	3.97
	$^3B_{3u}$	6.91	7.27	7.13	7.19	7.44
	$^3B_{1g}$	7.62	7.92	7.84	7.89	8.13
	^3A_g	8.00	8.32	8.16	8.22	8.48
	$^3B_{3u}$	8.49	8.94	8.73	8.79	9.05
MAD[b]		0.41	0.33	0.21	0.12	0.14
MAX[b]		0.77	0.85	0.48	0.53	0.52

[a] The optimized geometries from each DFT treatment are considered in these calculations. The open-shell systems are treated with the unrestricted Kohn-Sham formalism;

[b] The mean absolute deviation (MAD) and maximum absolute deviation (MAX) values are obtained with respect to the EE-EOM-CCSD(T)/aug-cc-pVTZ-mod data from Table I.

Table III: Excitation energies obtained with the eq. (4) by means of DFT calculations done with the aug-cc-pVTZ-mod basis set (in eV).[a]

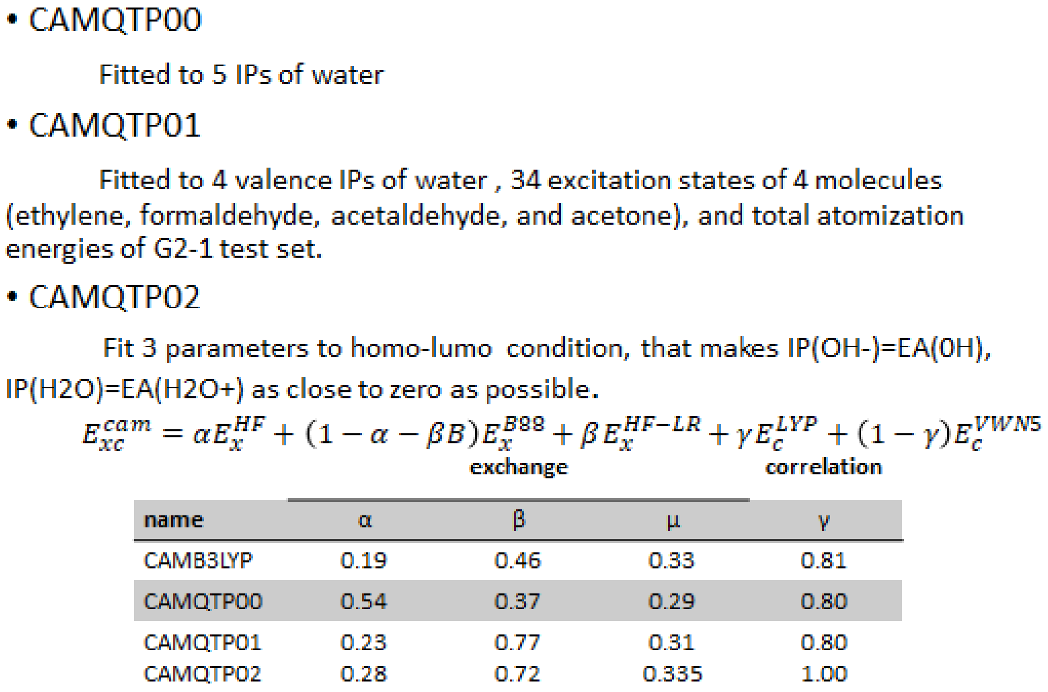
Molecule	State	CAM-B3LYP	CAM-QTP-00	CAM-QTP-01	CAM-QTP-02	LC-QTP
BeH ($^2\Sigma^+$)	$^2\pi$	-0.33	1.65	1.74	1.91	2.20
	$^2\pi$	4.69	5.93	6.01	6.06	6.28
BeF ($^2\Sigma^+$)	$^2\pi$	1.25	3.11	3.24	3.35	3.63
	$^2\Sigma^+$	4.08	5.59	5.72	5.78	6.02
	$^2\Sigma^+$	4.55	5.77	5.89	5.93	6.15
CO ($^1\Sigma^+$)	$^3\pi$	2.17	5.61	4.90	5.42	5.76
	$^3\Sigma^+$	8.13	10.40	10.08	10.31	10.62
	$^3\Sigma^+$	9.15	11.36	11.03	11.26	11.55
	$^3\pi$	9.36	11.52	11.15	11.38	11.64
N_2 ($^1\Sigma_g^+$)	$^3\pi_g$	3.61	7.52	6.48	7.08	7.38
	$^3\Sigma_g^+$	9.64	12.27	11.68	11.98	12.24
H_2CO ($^1A_1$)	$^3A_2$	0.13	3.42	2.70	3.16	3.40
	$^3B_2$	4.75	7.18	6.76	7.01	7.20
	$^3A_1$	5.92	8.22	7.81	8.03	8.19
	$^3B_2$	5.63	8.01	7.60	7.83	8.03
H_2O ($^1A_1$)	$^3B_1$	3.92	6.92	6.27	6.63	6.90
	$^3A_2$	6.04	8.99	8.33	8.67	8.89
	$^3A_1$	7.39	9.83	9.28	9.55	9.77
	$^3B_1$	7.54	9.97	9.42	9.68	9.90
CH ($^2\pi$)	$^2\Sigma^+$	3.80	6.14	5.87	6.10	6.41
	$^2\pi$	5.99	7.98	7.68	7.88	8.15
	$^2\Sigma^+$	5.75	7.83	7.58	7.79	8.08
	$^2\Sigma^+$	6.54	8.59	8.28	8.50	8.79
	$^2\pi$	7.18	9.09	8.85	9.03	9.31
	$^2\Sigma^+$	7.18	8.97	8.71	8.88	9.17
CH_3 ($^2A''_2$)	$^2A'_1$	3.47	5.56	5.43	5.62	5.96
	$^2A''_2$	5.47	7.26	7.08	7.24	7.54
NO ($^2\pi$)	$^2\Sigma^+$	3.42	5.85	5.37	5.62	5.83
	$^2\pi$	4.73	7.02	6.51	6.75	6.92
	$^2\Sigma^+$	4.70	7.05	6.54	6.79	6.97
	$^2\Sigma^+$	5.92	8.12	7.60	7.84	8.01
	$^2\pi$	6.33	8.45	7.90	8.14	8.30
	$^2\Sigma^+$	6.46	8.58	8.04	8.27	8.44
C_2H_4 (^1A_g)	$^3B_{1u}$	1.87	4.36	4.30	4.61	5.01
	$^3B_{3u}$	5.26	6.96	7.11	7.23	7.59
	$^3B_{1g}$	5.97	7.67	7.79	7.92	8.25
	^3A_g	6.57	8.05	8.19	8.28	8.60
	$^3B_{3u}$	6.98	8.57	8.69	8.80	9.14
MAD[b]		2.37	0.26	0.47	0.25	0.21

MAX[b]	4.53	1.05	1.67	1.07	0.77

[a] The optimized geometries of neutral molecules from each DFT treatment are considered in these calculations. The open-shell systems are treated with the unrestricted Kohn-Sham formalism;

[b] The mean absolute deviation (MAD) and maximum absolute deviation (MAX) values are obtained with respect to the EE-EOM-CCSD(T)/aug-cc-pVTZ-mod data from Table I.

The QTP parameters are summarized in the following Figure 11. Anyone can put these into their favorite KS-DFT program and obtain the kind of results we have shown in this report.



- CAMQTP00

  Fitted to 5 IPs of water

- CAMQTP01

  Fitted to 4 valence IPs of water , 34 excitation states of 4 molecules (ethylene, formaldehyde, acetaldehyde, and acetone), and total atomization energies of G2-1 test set.

- CAMQTP02

  Fit 3 parameters to homo-lumo condition, that makes IP(OH-)=EA(0H), IP(H2O)=EA(H2O+) as close to zero as possible.

$$E_{xc}^{cam} = \underbrace{\alpha E_x^{HF} + (1-\alpha-\beta B)E_x^{B88} + \beta E_x^{HF-LR}}_{\text{exchange}} + \underbrace{\gamma E_c^{LYP} + (1-\gamma)E_c^{VWN5}}_{\text{correlation}}$$

name	α	β	μ	γ
CAMB3LYP	0.19	0.46	0.33	0.81
CAMQTP00	0.54	0.37	0.29	0.80
CAMQTP01	0.23	0.77	0.31	0.80
CAMQTP02	0.28	0.72	0.335	1.00

Fig. 11.

Students graduated with Ph. D.’s in last five years.

Dr. Ann Melnichuk, PhD 2013, Intel,

Dr. Robert W. Molt, Jr., PhD 2013, ENSCO

Dr. Matthew Strasberg, PhD 2013. Space X

Dr. Varin Rishi, PhD 2017, Postdoc Va. Tech

Dr. Yifan Jin, PhD 2017, Postdoc Michigan State

Dr. Alex P Bazanté, Ph.D. 2017 Postdoc Va. Tech

Daniel C. Claudino, PhD, 2018 Postdoc Va. Tech

M. S. Karnamohit Ranka, MS 2016, Graduate Student.

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III. Publications supported by AFOSR, 2014-2018.

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2. A. Melnichuk and R.J. Bartlett, "Relaxed active space: Fixing tailored-CC with high order cluster. Part II. J. Chem. Phys. **140**, 064113/1-6 (2014).
3. P. Verma and R.J. Bartlett, "Increasing the applicability of DFT. IV. Consequences of ionization-potential improved exchange-correlation potentials," J. Chem. Phys. **140**, 18A534/1-11 (2014).
4. J.N. Byrd, V.F. Lotrich and R.J. Bartlett, "Correlation correction to configuration interaction singles from coupled cluster perturbation theory," J. Chem. Phys. **140**, 234108 (2014).
5. S. Maity, D. Parker, R. Kaiser, B. Ganoe, S. Fau, A. Perera, and R.J. Bartlett, "Gas-phase synthesis of boronylallene (H_2CCCH(BO)) under single -collision conditions: A crossed molecular beams and computational study," J. Phys. Chem. A **118**, 3810-3819 (2014).
6. D. Bokhan, D.N. Trubnikov, M. Musial and R.J. Bartlett, "Equation-of-motion coupled cluster method for ionized states with partial inclusion of connected triples: Assessment of the accuracy in regular and explicitly-correlated approaches," Chem. Phys. Letts. **610-611**, 173-178 (2014).
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13. J. Byrd, V. Rishi, A. Perera, and R.J. Bartlett, "Approximating electronically excited states with equation-of-motion linear coupled-cluster theory," J. Chem. Phys. **143,** 164103/1-9 (2015).

14. Y. Jin, A. Perera and R.J. Bartlett, “Spectroscopic analysis of diphosphatriazolate anion ($P_2N_3^-$) by coupled cluster methods as a step toward N_5^-,” Chem. Phys. Letts. **640**, 68-71 (2015).

15. D. Claudino, R. Gargano, and R.J. Bartlett, “Coupled-cluster based basis sets for valence correlation calculations,” J. Chem. Phys. **144**, 104106/1-11 (2016).

16. V. Rishi, A. Perera, and R.J. Bartlett, “Assessing the distinguishable cluster approximation based on the triple bond-breaking in the nitrogen molecule,” J. Chem. Phys. **144**, 124117/1-14 (2016).

17. D. Bokan, D.N. Trubnikov, and R.J. Bartlett, “Electric multipole moments calculation with explicitly correlated coupled-cluster wave functions,” J. Chem. Phys. **144**, 234107 (2016).

18. P. Verma and R.J. Bartlett, “Increasing the applicability of density functional theory. V. X-ray absorption spectra with ionization potential corrected exchange and correlation potentials,” J. Chem. Phys. **145**, 034108/1-14 (2016).

19. J.N. Byrd, J.J. Lutz, Y. Jin, D.S. Ranasinghe, J.A. Montgomery, Jr., A. Perera, X.F. Duan, L.W. Burgraf, B.A. Sanders, and R.J. Bartlett, “Predictive coupled-cluster isomer orderings for some Si_nC_m (m, $n \leq 12$) clusters: A pragmatic comparison between DFT and complete basis limit coupled-cluster benchmarks,” J. Chem. Phys. **145,** 024312 (2016).

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27. K. Ranka, A. Perera and R.J. Bartlett, “Elementary reaction profile and chemical kinetics study of $[C(^1D)/(^3P) + SiH_4]$ with the CCSD(T) method,” Chem. Phys. Letts. **680**, 61-68 (2017).

28. D.S. Ranasinghe, A. Perera, and R.J. Bartlett, “A note on the accuracy of KS-DFT densities,” J. Chem. Phys. **147**, 204103 (2017).

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30. R. L. A. Haiduke, R.J. Bartlett, “Non-empirical exchange-correlation parameterizations based on exact conditions from Correlated Orbital Theory,” J. Chem. Phys., **148**, 184106 (2018).

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32. J. Lutz, A. Perera, M. Nooijen, R. J. Bartlett, “Reference dependence of the two-determinant coupled-cluster method for triplet and open-shell singlet states of biradical molecules, J. Chem. Phys. **148**, 164102/1-11 (2018)

33. Y. Jin and R.J. Bartlett, “Accurate computation of X-ray absorption spectra with ionization potential optimized global hybrid functional,” J. Chem. Phys., **148**, 064111 (2018).

34. R. L. A. Haiduke and R. J. Bartlett “Can Excitation Energies be Obtained from Orbital Energies in a Correlated Orbital Theory?”, J. Chem. Phys., in press.

Book Chapters

1. A. Perera and R.J. Bartlett, “Geometric Metastability in Molecules as a Way to Enhance Energy Storage,” in *Advances in Quantum Chemistry*, volume 69, 147-170

2. J. Margraf and R.J. Bartlett, “Rigorous and Empirical Approaches to Correlated Single-Particle Theories,” in *Frontiers of Quantum Chemistry,* pp 1-20 (2018).

3. D. Claudino and R.J. Bartlett, “Basis Sets for Correlated Methods,” in *Lecture Notes in Chemistry*, (ed. E. Perlt) Springer (2017).

IV. Invited Lectures at Professional Conferences, under AFOSR sponsorship (2014-2018.

Mar 2018 - 255th National Meeting of the American Chemical Society, New Orleans, LA

Sep 2017 - 15th Central European Symposium on Theoretical Chemistry, Wisla, Poland

Aug 2017 - 11th Triennial Congress of the World Association of Theoretical and Computational Chemists, Munich, Germany

Aug 2017 – 254th National Meeting of the American Chemical Society, Washington, DC

June 2017 – International Academy of Quantum Molecular Sciences, Menton, France

May 2017 – Air Force Office of Scientific Research Contractors Meeting, Albuquerque,NM

Nov 2016 – 22nd Current Trends in Computational Chemistry, Jackson, MS

Oct 2016 – Workshop on Electron Correlation, Las Vegas, NV

July 2016 – International Society for Theoretical Chemical Physics (ISTCP-IX), Grand Forks, ND

June 2-16 – Molecular Quantum Mechanics (MQM) VIII, Uppsala, Sweden

Feb 2016 – Workshop Honoring Peter Schwerdtferger's 60th Birthday, Center for Theoretical Chemistry and Physics, New Zealand Institute for Advanced Study, Albany New Zealand

Dec 2015 – 2015 International Chemical Congress of Pacific Basin Societies (Pacifichem), Honolulu, HI

Nov 2015 – 67th Southeastern and 71st Southwestern Regional Meeting of the American Chemical Society, Memphis, TN

May 2015 – Frontiers in Electronic Structure Theory, a meeting in honor of Sourav Pal's 60th Birthday, Goa, India

May 2015 - Air Force Office of Scientific Research Contractors Meeting, Albuquerque, NM

May 2014 – FAME (Florida Annual Meeting & Exhibitions) 2013, Computational Chemistry Symposium, Tampa, FL

October 2014 – 10th Triennial Congress of World Association of Theoretical and Computational Chemists (WATOC), Santiago, Chile

March 2014 – 25th Austin Symposium on Molecular Structure and Dynamics, Dallas, TX

Invited Colloquia Presented at Universities and Laboratories

September 2016 – Department of Chemistry, The Johns Hopkins University, Baltimore, MD

June 2016 – Center for Theoretical and Computational Chemistry, University of Oslo, Oslo, Norway

May 2018 – Department of Chemistry, Michigan Technological University, Houghton, MI

June 2018 – Department of Chemistry, The University of Texas at San Antonio, San Antonio, TX