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Journal

The Journal of Chemical Physics, 153(15)

ISSN

0021-9606

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Publication Date

2020-10-21

DOI

10.1063/5.0020595

Peer reviewed

Core Excitations with Excited State Mean Field and Perturbation Theory

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(Dated: 3 July 2020)

We test the efficacy of excited state mean field theory and its excited-state-specific perturbation theory on the prediction of K-edge positions and X-ray peak separations. We find that the mean field theory is surprisingly accurate, even though it contains no accounting of differential electron correlation effects. In the perturbation theory, we test multiple core-valence separation schemes and find that, with the mean field theory already so accurate, electron-counting biases in one popular separation scheme become a dominant error when predicting K-edges. Happily, these appear to be relatively easy to correct for, leading to a perturbation theory for K-edge positions that is lower scaling and more accurate than coupled cluster theory and competitive in accuracy with recent high-accuracy results from restricted open-shell Kohn Sham theory. For peak separations, our preliminary data show excited state mean field theory to be exceptionally accurate, but more extensive testing will be needed to see how it and its perturbation theory compare to coupled cluster peak separations more broadly.

I. INTRODUCTION

X-ray-induced core excitations are probably the most extreme example of post-excitation orbital relaxations under regular theoretical study.¹ With core shielding greatly reduced, the valence electrons contract substantially following the excitation, which means that methods attempting to predict core excitation energies face a challenge in getting even the mean-field orbital description right before even worrying about whether the correlation treatment is balanced between ground and excited states. Unlike charge transfer excitations, where orbital relaxations are important but “only” have a few eVs of energetic impact, orbital relaxations for core excitations can change energies by 10 eV or more, as shown for example in the difference between simple configuration interaction singles (CIS) and non-orthogonal CIS (NOCIS).^{2,3} From this perspective, it is not too surprising that high-level correlation treatments like equation of motion (EOM) coupled cluster⁴⁻⁷ and algebraic diagrammatic construction (ADC)^{8,9} often see errors greater than an eV when predicting the position of the K-edge. While these methods have sophisticated correlation treatments, their ability to relax the orbitals, although present, is limited. For example, in EOM coupled cluster with singles and doubles (EOM-CCSD), orbital relaxations come from the doubles part of the configuration interaction coupling to the primary single excitation,¹⁰ and so only the first term in the Taylor expansion of a proper unitary orbital rotation is present. Given the high cost scaling of high-level correlation treatments and the fact that their correlation sophistication may be hidden by incomplete orbital relaxation, it seems worthwhile to explore methods that work first to fully relax the orbitals and only then worry about correlation.

The most well-known example of full orbital relaxation is the Δ SCF family of approaches,^{11,12} in which an open-shell Slater determinant’s orbitals are relaxed by finding the energy stationary point corresponding to the desired state. As

Hartree-Fock-based Δ SCF (Δ SCF/HF) often makes K-edge errors of multiple eV,² one would at first glance expect to get down to errors of an eV or less only when differential electron correlation is accounted for. However, things are not necessarily better when moving to density functional theory (DFT) based Δ SCF, in which full orbital relaxation is paired with a state-specific correlation treatment. Indeed, K-edge errors are still often above an eV and can be strongly functional dependent.² Very recently, the imposition of approximate spin symmetry (approximate in that there is no actual wave function to be spin-symmetric) via the restricted open-shell Kohn Sham (ROKS) approach has been shown to offer much greater accuracy in K-edge prediction for some functionals.¹³ This success begs a question: is the improvement due to the effect of spin-symmetry on the orbital relaxation, its effect on the correlation treatment, or both? As we will see below, it would appear that, once spin symmetry is fully in place, even a correlation-free mean field treatment of the K-edge becomes accurate to better than an eV. Thus, although differential correlation effects are critical for very high accuracy, it is not clear that they are the correct explanation for why many Δ SCF approaches commonly error by multiple eV.

When one does turn to correlation treatments, difficulties related to valence continuum coupling becomes a key issue. Very often, quantum chemistry methods separate themselves from the continuum using the concept of core-valence separation (CVS),¹⁴ which has a variety of practical realizations^{4,5,15-18} that are not entirely equivalent to each other.¹⁹ Some “strong” CVS approaches disable all core-valence correlation,^{5,15-18} which is the analogue of the ground state frozen core approximation. Others^{4,15,16} disable only the correlation terms corresponding to the Auger processes that are responsible for the actual coupling to the valence continuum. For example, the difference between the popular CVS-ADC(2) and CVS-ADC(2)-x schemes is the treatment of doubly core excited components of the wave function.¹⁶ Although the strong separation approaches are somewhat simpler, they create a situation in which more electrons are being correlated in some states as compared to others, an issue that we will discuss in some detail below.

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In this study, we explore the efficacy of excited state mean field (ESMF) theory^{20–23} and its excited state analogue (ESMP2)^{20,21,24} to ground state Møller Plesset theory for the prediction of core excitation energies. Like Δ SCF and ROKS, ESMF offers full orbital relaxation at a cost scaling equivalent to ground state Hartree Fock theory. In fact, its practical cost can be as low as a factor of two when compared to Hartree Fock thanks to the recent development of a self consistent field formulation of the theory.²³ Unlike Δ SCF and ROKS, ESMF contains an explicit ansatz that is rigorously spin-symmetric, which, based on the results presented below, seems to matter a good deal in allowing it to outperform Δ SCF/HF. As with other post-mean-field correlation treatments, a CVS approach makes ESMP2 much simpler to apply to core excitations. However, there is some question as to what the ideal CVS approach to ESMP2 is, given that cancellation of error is key and that most methods we can compare to do not start from a fully orbital-relaxed reference, raising the concern that what makes for good error cancellation elsewhere may or may not be effective for ESMP2. As we will see, ESMF is accurate enough on its own that some choices of CVS for ESMP2 fail to make it more accurate than the uncorrelated reference state!

II. THEORY

A. The Single-CSF Reference

In this study, we restrict ourselves to a simple excited state reference function in order to simplify our choices for CVS, and because good accuracy can be achieved even with this simple choice. Specifically, our reference will be one singly-excited singlet-paired configuration state function (CSF) whose orbitals are optimized state-specifically. Note that this reference is equivalent to an ESMF wave function whose configuration interaction coefficients are all zero except for the up- and down-spin versions of one particular occupied-to-virtual promotion. It can also be seen as a two-orbital restricted active space (RAS) wave function, or as a spin-pure generalization of the Δ SCF approach.

In practice, preparing this single-CSF reference for a particular excited state involves selecting an initial orbital basis (we start with restricted Hartree Fock orbitals), choosing which occupied-to-virtual transition within this basis will be used for constructing the initial CSF, and then relaxing the orbitals so that the energy becomes stationary with respect to further orbital rotations. For the basis and states investigated here, we find that the recently-introduced self consistent field ESMF approach²³ converges healthily without collapsing to a different state. That said, there doubtless are cases where, as in ground state Hartree Fock, this self consistent field approach will either fail to converge or converge to wrong stationary point. In particular, we expect to face convergence problems for higher-lying states with significant Rydberg character. In such cases, the quasi-Newton minimization of a generalized variational principle²¹ can be used to ensure convergence to the correct state. Again, in the present study, this was not

necessary, allowing us to benefit from the remarkably higher efficiency²³ of the self consistent field approach.

B. ESMP2 and the choice of CVS

In this study we will rely on the recently-introduced N^5 -scaling version of ESMP2.²⁴ To decouple the theory from the valence continuum, we will test two approaches to CVS, both of which are closely related to CVS schemes that have been employed in other theories. One approach is to disable only out-of-reference transitions that correspond to Auger processes, as these terms are often small in magnitude⁴ and are the only terms that create numerical difficulties by coupling to the valence continuum. For ground state MP2, which we use when evaluating ESMP2 excitation energies, this implies that no orbitals are frozen, and so this Auger-only-CVS (Ao-CVS) means keeping all terms in Figure 1 and all the terms in the “enabled” box of Figure 2. This approach is very similar to that used by Coriani and Koch,⁴ where the energetic effect of putting the Auger terms back was typically below 0.1 eV. These results agree with our finding that, if one enables the Auger terms, then in the aug-cc-pCVTZ basis at least ESMP2 can in some cases be converged and gives an energy less than 0.1 eV different than the more stable Ao-CVS-ESMP2 approach.

A second CVS approach is to disable all out-of-reference transitions that change the number of electrons in the core. This “strong” CVS (S-CVS) approach is based on the idea¹⁴ that the coulomb repulsion integrals that create these transitions are small due to the small spatial overlaps between core and valence orbitals. Setting these integrals to zero is equiv-

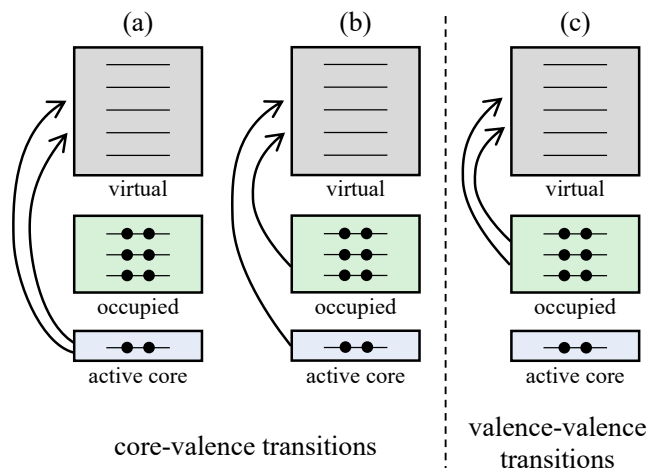


FIG. 1: Classes of post-RHF excitations that can contribute to the MP2 energy. The Ao-CVS approach retains all of these terms, while the S-CVS approach disables the core-valence terms. Note that excitations out of core orbitals that are doubly occupied in the reference CSF are neglected in both the ground and excited state for S-CVS, but included in the ground and excited state for Ao-CVS.

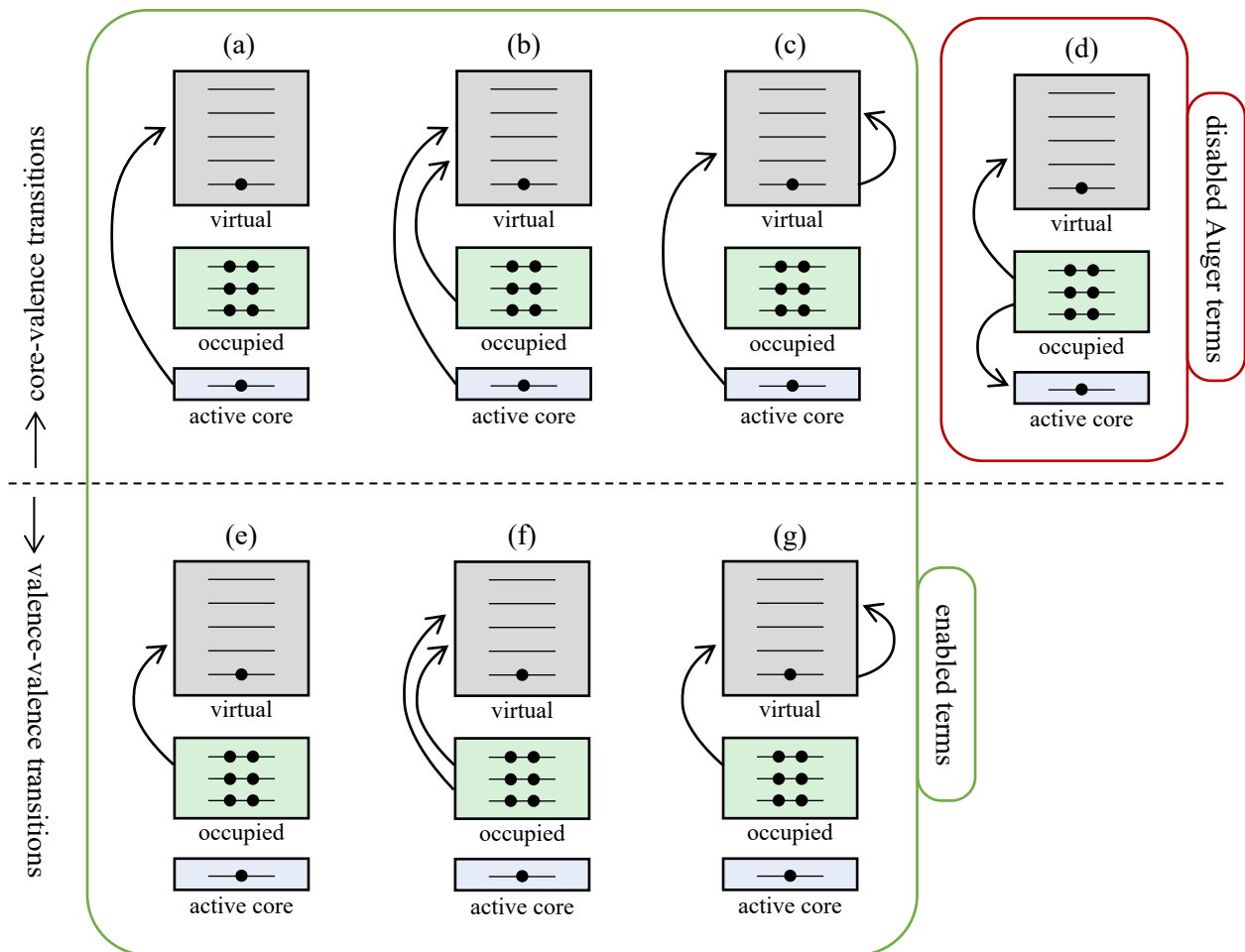


FIG. 2: Classes of post-ESMF excitations that can contribute to the ESMP2 energy when the ESMF state is limited to a single core-excited CSF. In S-CVS, we retain only the valence-valence terms, and core orbitals that are doubly occupied in the reference CSF are frozen during the correlation treatment. In Ao-CVS, we retain all terms in the “enabled” box, and core orbitals that are doubly occupied in the reference CSF are treated the same as doubly occupied valence orbitals.

alent to disabling all terms on the core-valence side of the dashed lines in Figures 1 and 2. Comparing to the recent Linear-Response Density Cumulant Theory work of Sokolov *et al.*,¹⁵ our S-CVS is similar to their CVS-ODC-12-a scheme in which their Hessian space is restricted to containing only elements with exactly one core excitation and up to one additional valence excitation. Our Ao-CVS approach, on the other hand, is analogous to CVS-ODC-12-b in that it allows additional excitations out of the active edge core. As we will see in the results, the difference between our schemes is typically about 1 eV, which is quite similar to the difference between their two schemes. Although this type of strong CVS approach has been used with significant success for predicting peak separations in the fc-CVS-EOM-CCSD work of Vidal and coworkers,⁵ we find that it does introduce a noticeable bias towards lower K-edge energies due to the fact that the excited state calculations are now correlating one more electron than the ground state calculations. Although this bias does not seem to effect energetic separations between peaks, there is a

relatively simple way to counteract its effect on K-edge prediction. As the issue is that we are correlating an extra electron in the excited state vs the ground state, we simply need a rough estimate for that extra correlation energy. To get this estimate, we should account for i) the valence electrons in the excited state experiencing a higher effective nuclear charge and ii) the fact that the extra electron is in a singly occupied orbital, and will thus bring somewhat different correlations with it than those seen in doubly occupied orbitals. One approach that accounts for both of these effects is to evaluate *part* of the valence correlation energy of the equivalent-core-approximation^{25,26} cation formed by replacing the nucleus in question by the one with the next higher charge, e.g. $C \rightarrow N$. In particular, we sum only the terms in MP2 in which the occupied indices are distinct and both in the valence orbitals. This inter-orbital correlation energy is then divided by the number of valence electrons and subtracted from our S-CVS-ESMP2 correlation energy as a correction to counteract the effect of having an additional correlated electron relative

to the ground state. Note that this corrected S-CVS (CS-CVS) approach has no effect on peak separations, and so if the plan is to shift the predicted spectrum to line it up with experiment, then CS-CVS will have no effect. Instead, it is intended as a way to improve predictions of K-edge transition energies. In future, more sophisticated correlation treatments may allow for greater insight into how this electron counting bias is best addressed, but for now we will rely on the simple after-the-fact correction discussed above.

C. Artificial Core Hole Localization

Having chosen a single-CSF reference, it is important to recognize that our approach is unable to treat symmetry-delocalized core holes in a fully rigorous manner. To take ethylene as an example, the true core excited state contains by symmetry two components, one with the core hole on the left carbon and the other with the core hole on the right. As in any core excited state, the valence orbitals relax strongly by contracting towards the hole, but as the two components of the wave function have the hole in different locations, they experience different relaxation effects. In other words, the behavior of the valence electrons is strongly dependent on the positions of the three remaining core electrons, which is a strong electron correlation. Like ground state mean field theory, ESMF theory does not contain such correlations, and so as a reference it is qualitatively incorrect for such states. Note that this is true whether ESMF is used in its full multi-CSF form or in the limited single-CSF form used here. Instead, to be qualitatively correct, the reference would need to build in these strong correlations, as is accomplished for example by the NOCIS approach.²

Although we will show below the poor results that come from blindly applying ESMP2 to such states, there is a relatively simple workaround. As the energy difference between the true hole-delocalized excited state and the similar broken-symmetry state (in which the hole is localized on one site) is typically small,¹³ we can construct a practical approach to predicting these state’s energies by providing our self consistent ESMF optimization with a hole-localized initial guess. After identifying the gerade and ungerade 1s Hartree Fock orbitals, we can prepare an initial guess for our core hole by taking either the plus or minus combination. Upon optimizing ESMF, we find in all cases studied here that the SCF procedure keeps the hole localized, and although this is qualitatively incorrect, it does not appear to have any adverse effects when evaluating the ESMP2 correlation energy. In the ground state calculations for the two CVS schemes, we note that we are either freezing both the gerade and ungerade orbitals (S-CVS) or freezing neither of them (Ao-CVS), and so we need make no alteration in how the ground state correlation calculations are done for these states.

III. RESULTS

A. Comparing methods

Before discussing results for ESMP2 and the two CVS schemes, let us first consider the accuracy of our orbital-relaxed ESMF reference wave function on its own. As seen in Table I, this single-CSF ansatz predicts K-edges mostly within 1 eV of experiment, with a mean unsigned error of 0.6 eV. This result shows that correlation effects cancel in the K-edge energy difference to a very significant degree. Remarkably, this mean unsigned error for ESMF — which offers no treatment of weak correlation effects — is slightly better than what was achieved by Δ SCF/B3LYP and Δ SCF/MP2, both of which show mean unsigned errors between 0.6 eV and 0.7 eV for the K-edge values in Table 2 of Gill et al.¹² While one might expect the formal similarities between ESMF and Δ SCF/HF to lead to similar overall accuracy, Δ SCF/HF errors are often in the 2 to 3 eV range,² even when we leave aside molecules with delocalized core holes. We therefore see that the slightly more complex two-determinant ESMF reference is, in this context at least, well worth the trouble. Another approach with significant similarity to ESMF is NOCIS, in which orbital relaxations are approached by restricted open-shell Hartree Fock calculations on the relevant cations. While its K-edge errors are dramatically smaller than those of orbital-unrelaxed CIS,² they are larger than those for ESMF, which further emphasizes the value of fully state-specific orbital relaxations. Of the six functionals tested with ROKS in recent work by Hait and Head-Gordon,¹³ only the SCAN and ω B97X-V functionals lead ROKS to meaningfully better performance than ESMF in terms of mean unsigned error. In terms of K-edge energetics, we therefore see that ESMF’s approach of spin-symmetric, fully-state-specific orbital relaxation coupled with a complete neglect of weak correlation effects out-performs NOCIS and Δ SCF/HF and is comparable to or better than most approaches that include weak correlation treatments. One begins to wonder whether the post-ESMF cost of ESMP2 is going to be worth the trouble.

To find out, let us begin by considering the S-CVS approach to ESMP2, which tends to underestimate the K-edge as shown in Table I. To understand why, consider the number of electrons being correlated in the ground and excited state calculations. In the ground state, S-CVS is simply the frozen core approximation, and so the number of correlated electrons is equal to the number of valence electrons. In S-CVS-ESMP2, however, there is an additional valence electron, so although the core is still frozen, the number of electrons being correlated is one larger than in the ground state. If one considers that an electron pair’s correlation energy is on the order of 1 eV, and that one electron is half of a pair, a simple electron counting argument seems to explain the underestimation. Our CS-CVS approach, which attempts to correct for this bias in a molecule-specific manner by parsing MP2 contributions in the one-higher-core-charge cation, does manage to improve the K-edge predictions overall, but it is clearly more effective for the C K-edge than for the others.

Turning now to Ao-CVS, we see in Table I that it’s K-edges

TABLE I: K-Edges (eV) for small molecules. The atom in bold is the active edge. Estimated relativistic corrections²⁷ were added to all calculated excitation energies (0.10, 0.21, 0.38, and 0.64 eV for C, N, O, and F, respectively). The geometries were set to their experimental values as given in the CCCBDB. The basis set is aug-cc-pCVTZ.

Molecule	Exp.	ESMP2			
		ESMF	S-CVS	CS-CVS	Ao-CVS
CH ₄	288.0 ²⁸	0.5	-0.7	-0.2	0.3
C ₂ H ₂	285.8 ²⁹	0.7	-0.8	-0.1	0.3
C ₂ H ₄	284.7 ²⁹	0.7	-0.8	-0.1	0.3
C ₂ H ₆	286.9 ³⁰	0.5	-0.9	-0.3	-0.3
HCN	286.4 ³¹	0.7	-0.6	0.1	0.5
C ₂ N ₂	286.3 ³¹	0.8	-0.5	0.3	0.6
CO	287.4 ²⁹	0.8	-1.1	-0.2	0.0
CO ₂	290.8 ²⁹	1.3	-1.0	0.0	0.1
H ₂ C O	285.6 ³²	0.9	-0.4	0.4	0.7
CH ₃ O H	287.9 ³³	1.1	-0.4	0.4	0.2
NH ₃	400.7 ²⁸	0.4	-0.8	-0.2	-0.6
N ₂	400.9 ³⁴	0.5	-0.4	0.4	0.6
NNO	401.1 ³⁴	0.3	-0.6	0.4	0.5
NNO	404.7 ³⁴	0.4	-0.3	0.7	0.7
HCN	399.7 ³¹	0.4	-0.5	0.2	0.6
C ₂ N ₂	398.9 ³¹	0.7	-0.5	0.3	0.6
H ₂ O	534.0 ²⁸	0.3	-0.5	0.2	-0.3
CO	534.2 ²⁹	-0.2	-0.4	0.2	0.7
CO ₂	535.3 ³⁵	0.4	-0.3	0.5	0.8
NNO	535.1 ³⁵	-0.5	-0.6	0.3	0.5
H ₂ CO	530.8 ³²	0.0	-0.5	0.2	0.6
CH ₃ O H	534.1 ³³	0.3	-0.4	0.3	0.1
HF	687.4 ³⁶	0.1	-0.2	0.5	0.1
F ₂	682.2 ³⁶	-0.8	-0.3	0.5	0.3
Mean Signed Error		0.4	-0.6	0.2	0.3
Mean Unsigned Error		0.6	0.6	0.3	0.4
RMS Error		0.6	0.6	0.3	0.5
C	Signed Error	0.8	-0.7	0.0	0.3
	Unsigned Error	0.8	0.7	0.2	0.3
N	Signed Error	0.5	-0.5	0.3	0.4
	Unsigned Error	0.5	0.5	0.4	0.6
O	Signed Error	0.1	-0.4	0.3	0.4
	Unsigned Error	0.3	0.4	0.3	0.5
F	Signed Error	-0.3	-0.2	0.5	0.3
	Unsigned Error	0.5	0.2	0.5	0.3

are typically more accurate than those of S-CVS, but not as accurate as those of CS-CVS. Note that, as Ao-CVS correlates all electrons in both the ground and the excited state, there are no correlation adjustments to be made based on counting arguments. While the K-edges suggest that Ao-CVS and CS-CVS do have something to offer over ESMF, the peak separations shown in Table II are a different story. Once one accounts for the fact that the half-eV error for ammonia’s $5a_1/3p$ state is almost entirely due to the fact that our basis lacks extra Rydberg functions,⁵ ESMF is more accurate for this small initial sample of peak separations than any of the ESMP2 CVS variants. Indeed, it is, in this Rydberg-deficient basis, on par

TABLE II: Peak separations (eV) in methane, ammonia, and water. Experimental numbers are the peak separations between the lowest-lying core excited state and higher-lying states, with methane’s lowest core excited state adjusted to remove the v_4 vibrational quanta.³⁷ Theoretical numbers are errors relative to the experimental peak separations, with S-CVS and CS-CVS (as they are identical for separations) reported together as (C)S-CVS.

Transition	Exp.	ESMP2			
		ESMF	(C)S-CVS	Ao-CVS	
CH ₄ $3a_1/3s \rightarrow 2t_2/3p$	1.30	0.00	0.19	0.90	
NH ₃ $4a_1/3s \rightarrow 2e/3p$	1.67	-0.01	0.18	1.07	
$4a_1/3s \rightarrow 5a_1/3p$	2.20	0.51	0.78	1.65	
OH ₂ $4a_1/3s \rightarrow 2b_2/3p$	1.89	-0.01	0.10	1.06	

with recent equation of motion coupled cluster work,^{4,5} which is quite remarkable given its complete neglect of the correlation details. Ao-CVS-ESMP2, on the other hand, is especially poor for these peak separations, biasing the energies of the higher states up by about 1 eV, which calls for some analysis. In looking at the various contributions to the Ao-CVS-ESMP2 correlation energy, we find that a key difference between the (lower) totally symmetric s states and the (higher) not-totally-symmetric p states in Table II is found in the ESMP2 energy contribution from the the determinant in which the second core electron has been promoted to join its partner in the reference CSF’s singly-occupied virtual orbital. This determinant is totally symmetric in these molecules, and so cannot make any energy contribution to the p states. In the s states, however, this Figure-2-type-(a) determinant contributes about 1 eV of correlation energy, which accounts for the 1 eV bias against the p states that we see but does not quite explain it. The answer may lie in the excitations that this N^5 -scaling version of ESMP2 leaves out.²⁴ Many of these neglected excitations are core-valence in nature, and so the present implementation of Ao-CVS-ESMP2 may be biased by its lack of these core-valence terms. However, in our experience with valence excitations at least, we have yet to see these terms have any appreciable effect.²⁴ The S-CVS and CS-CVS approaches, in contrast, neglect all core-valence terms, which according to the current results is substantially less biased when evaluating peak separations. In sum, the CS-CVS approach appears preferable to ESMF for evaluating the K-edge position, but it is not obvious that any version of ESMP2 is preferable to ESMF when evaluating peak separations, especially considering that ESMF can now be run for a near-Hartree-Fock cost.²³

As a final note on accuracy before we turn our attention to periodic trends, Table III shows that both ESMF and ESMP2 do indeed perform quite poorly if the core orbital is delocalized. Again, the reason for this failure is that the mean field reference does not contain the strong correlations inherent to how the valance electron’s contractions are dependent on the positions of the remaining core electrons. While one can cheat by artificially localizing the core hole without much effect on accuracies in the molecules studied here, this formal failure

TABLE III: Comparison of localized- and delocalized-hole approaches for the acetylene K-edge in the aug-cc-pCVTZ basis. The hole is either delocalized in the gerade (g) or ungerade (u) 1s orbital, or localized on left (L) or right (R). The experimental edge lies at 285.8 eV.²⁹

	ESMF	S-CVS	Ao-CVS
L	286.4	285.0	286.0
R	286.4	285.0	286.0
g	294.1	292.5	293.0
u	294.0	292.4	293.0

of the theory may well cause more serious problems in other delocalize-core-hole situations. Certainly the electron density it predicts will be biased towards one side and will fail to respect symmetry, which will for example create a permanent dipole moment where one should not exist.

B. Periodic trends

Another interesting aspect of the K-edge results of Table I is the periodic trends they contain. All else being equal, the per-electron correlation energy for valence electrons rises as one moves from lighter (C) to heavier (F) elements, which one can verify by simple frozen core MP2 calculations on CH₄, NH₃, OH₂, and FH. As the valence electrons in a core excited state experience an effective nuclear charge that is one higher than in the ground state, the natural scale of valence correlation energy is larger in the K-edge state. With ESMF neglecting all correlation outside the (sub-0.1eV) spin recoupling energy, we would therefore expect it to error high for K-edges, which is exactly what we see. Further, as the relative effective change in core charge is larger in lighter atoms (e.g. C→N grows the formal charge by 7/6 while F→Ne grows it by only 10/9) we would expect ESMF’s tendency to error high to be stronger in lighter atoms, as these experience a larger relative jump in valence correlation energy scale upon core excitation. Again, this is what we see.

Another clear trend is that S-CVS’s expected underestimation of K-edges gets smaller as the K-edge element gets heavier. As with ESMF’s tendency to over-estimate, one can try to rationalize this trend based on lighter elements having larger jumps in the valence correlation energy scale upon K-edge excitation. As S-CVS is correlating an extra electron compared to the ground state, and since this correlation is happening on the excited state’s (larger) correlation energy scale, one might argue that the fact that the excitation-induced jump in this scale is larger in light elements explains why S-CVS has a larger negative K-edge bias in lighter elements. However, the fact that the correction we make in CS-CVS has essentially the same scale (0.7 to 0.8 eV on average) for the different elements’ K-edges suggests that there may be a second effect contributing to the trend in the S-CVS K-edge energy biases.

IV. CONCLUSION

We have investigated the ability of excited state mean field theory and an accompanying excited-state-specific perturbation theory to predict K-edge energies and peak separations for core excited states. Our most remarkable finding is that, despite its blanket neglect of correlation energy, excited state mean field theory is typically within 1 eV for K-edge energies and even more accurate in a preliminary test on peak separations. Indeed, for the latter, it is more accurate than the associated perturbation theory and competitive with equation of motion coupled cluster, emphasizing how large a role correlation energy cancellation plays in these predictions. By correcting the electron-counting bias inherent to one of our perturbation theory’s core-valence separation schemes, we find that the perturbation theory can out-perform the mean field theory for predicting the position of the K-edge, and indeed appears to outperform most other available methods in this regard. The only available method that seems to do significantly better is restricted-open-shell Kohn Sham theory, and then only when the SCAN functional is employed. In cases where self-interaction errors in the valence orbitals are a concern (e.g. in a molecule where the LUMO and LUMO+1 are spatially separate and similar but not degenerate in energy), the perturbation theory presented here may be clearly preferable, especially given that its N^5 cost scaling is lower than the N^6 scaling of coupled cluster theory.

Looking forward, there are multiple opportunities and priorities for further development. For starters, the after-the-fact correction we use to counteract our core-valence separation’s electron counting bias is clearly not unique. In future, it could be more satisfying and predictive to perform a more in-depth analysis of the different ESMP2 contributions to the excited state energy. It may for example be possible to identify and explicitly disable terms that correspond to the electron counting bias. In excited state mean field theory, a more efficient implementation of the quasi-Newton minimization of generalized variational principles would be especially helpful for states with Rydberg character, as the self-consistent field approach, although fast, is often not stable once extended Rydberg functions are added to the basis. Thinking of perturbation theory’s wide existing role in supporting other methods, it may also be interesting to develop ESMP2 natural orbitals as a starting point for local correlation methods and to test the efficacy of ESMP2 as a black-box (i.e. no active space needed) generator of multi-Slater expansions in core-excited quantum Monte Carlo. Finally, given the efficacy of restricted open-shell Kohn Sham and the remarkable difference in accuracy between Hartree-Fock-based Δ SCF and our excited state mean field theory, it would be especially interesting to investigate whether density functional extensions³⁸ to this mean field theory can combine the best of both worlds.

Acknowledgments — This work was supported by the Office of Science, Office of Basic Energy Sciences, the U.S. Department of Energy, Contract No. DE-AC02-05CH11231. Calculations were performed using the LBNL Lawrence Livermore computing cluster.

Data Availability Statement — The data that supports the findings of this study are available within the article.

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