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Unraveling the variational breakdown of core valence separation calculations: Diagnostic and cure to the over relaxation error of double core hole states

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The core valence separation (CVS) approximation is the most employed strategy to prevent the variational collapse of standard wave function optimization when attempting to compute electronic states bearing one or more electronic vacancies in core orbitals. Here, we explore the spurious consequences of this approximation on the properties of the computed core hole states. We especially focus on the less studied case of double core hole (DCH) states, whose spectroscopic interest has recently been rapidly growing. We show that the CVS error leads to a systematic underestimation of DCH energies, a property in stark contrast with the case of single core hole states. We highlight that the CVS error can then be interpreted as an over relaxation effect and design a new correction strategy adapted to these specificities.

I. INTRODUCTION

The variational principle is one of the cornerstones of many quantum chemistry methods. In practice, it allows to reframe the solving of eigenvalues equations as a, computationally much simpler, optimization problem. However, variationality can become a critical pitfall when attempting to reach high lying eigenstates. Indeed, one has to either, climb the variational ladder, one state at a time, or, to bias the optimization in order to avoid the variational collapse onto lower lying eigenstates. While the first strategy can be applied when the targeted states remain close to an edge of the eigenvalue spectrum, this approach become quickly impracticable and one is left with the second option.

Calculation of electronic states bearing inner shell vacancies stand among the most important challenges for the application of quantum chemistry methods since such states are at the root of many core electron based spectroscopies such as X-ray absorption (XAS/NEXAFS) and single core hole (SCH) X-ray photoelectron spectroscopy (XPS). Moreover, the recent interest for emerging double core hole (DCH) states spectroscopies [1–11] has been rapidly growing thanks to improved light sources and detectors [12–19] eventually leading to even more demanding simulations.

Core hole states calculation is one such case where the variational principle needs to be circumvented. Indeed, these are highly excited states of either, the neutral system (core excited), or of the cationic one (core ionized). Due to their high energy, molecular core hole states are embedded in ionization continua corresponding to ejection of outer shells electrons. Such couplings will not be considered here, as they are usually neglected in computational approaches dedicated to core hole states resulting in what is sometimes referred to as a *diabatized* representation of the physical problem [20].

Following standard wave function based strategies, one has to avoid variational pitfalls on two occasions. First, when optimizing the molecular orbital (MO) basis for the core hole state of interest, and then, when performing the actual wave function optimization. The most common strategy employed to optimize MO for core hole states is the maximum overlap method (MOM) [21, 22] that consists in a biased self consistent field (SCF) procedure in which the Slater determinant built at each iteration do not follows the aufbau principle. In practice, the occupied/virtual status of each MO is not defined by their relative eigenvalues but *via* an overlap criterion with the set of occupied orbitals of the previous iteration. Alternative strategies include, freezing the core orbital bearing the vacancy and optimizing the remaining MOs under that constraint [23, 24], optimizing the orbitals in the field of an increased atomic charge mimicking the effects of the core shell vacancy (core equivalent model) [25–27] as well as general optimization schemes for excited states [28–30].

The main focus of the present article is the Core Valence Separation (CVS) approximation often used to prevent the variational collapse of core hole states' wave functions. Initially introduced by Cederbaum *et al.* for SCH [31] and later extended to DCH [4, 32], it consists in neglecting the weak coupling between configurations with different occupation number of the core MOs. This leads to the isolation of core hole CVS Hamiltonians which can be diagonalized to yield approximate core hole states. This strategy have been adapted to a large

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variety of methods [10, 20, 33–47]. Due to its almost mandatory character, the CVS approximation is thus one of the most critical aspect of core hole state calculations.

In this paper, we present an in-depth exploration of the spurious consequences of the CVS approximation especially focusing on the less explored case of double core hole states. Following this introduction, the second section of this paper is dedicated to summarize the general aspect of the CVS approximation and to illustrate its limits. In particular, we show that the CVS error can be interpreted as an over-relaxation effect induced by the partial breakdown of the variational constraint. We also highlight that it leads to non negligible error on excited state properties, a fact generally overlooked. Then, in the third section, we discuss the characteristics of the few computational strategies that have been proposed to attenuate the drawbacks of the CVS approximation and we propose a variational method taking into account our new insight on the nature of this error.

All results (unless extracted from the literature) were computed using Quantum Package 2.0 [48] and our homemade series of plugins.

II. THE CVS APPROXIMATION

A. Principle of the approximation

1. *Variational calculation of excited states*

Within the framework of a variational method, one can exactly compute any given eigenstate $|\Psi_n\rangle$, being granted that $\{\overset{<}{\Psi}_n\}$, the set of eigenstate of lower energy than the targeted state, is perfectly known. One can then minimize the energy of a trial wave function under an orthogonality constraint with respect to this set. Thus,

$$|\Psi_n\rangle = \arg\left(\min_{\varphi_\mathrm{e}\perp\{\overset{<}{\Psi}_n\}}\left[\langle\varphi_\mathrm{e}|\hat{H}|\varphi_\mathrm{e}\rangle\right]\right), \tag{1}$$

where φ_e is the trial function, and "arg" represents the argument *i. e.* the minimizing function. However, as exact calculations are almost always out of reach, restrictions are applied to reduce the variational flexibility of the calculation, and thus, the region of the Hilbert space that can be explored. As a result one only computes approximated eigenstates, here denoted as $|\widetilde{\Psi}_n\rangle$. As a result of their approximated nature, each $|\widetilde{\Psi}_n\rangle$ formally develop onto the full set of exact eigenstates,

$$|\widetilde{\Psi}_n\rangle = \sum_m C^n_m \times |\Psi_m\rangle\,. \tag{2}$$

Under appropriate conditions, one expect for $|\widetilde{\Psi}_n\rangle$ to be as good an approximation to $|\Psi_n\rangle$ as possible. It then comes that,

$$\langle\widetilde{\Psi}_n|\Psi_n\rangle = C^n_n \approx 1 \quad \text{and} \quad \widetilde{E}_n \approx E_n. \tag{3}$$

When attempting to compute excited states that lie too high to be reached by a standard *climb the ladder* type approach, one may try to find restriction of the variational flexibility of the calculation such that the approximated states computed cannot collapse onto lower lying eigenstates. In another word, one may try to enforce that,

$$|\widetilde{\Psi}_n\rangle = \sum_{\Psi_l\in\{\overset{<}{\Psi}_n\}} 0\times|\Psi_l\rangle + \sum_{\Psi_m\notin\{\overset{<}{\Psi}_n\}} C^n_m \times |\Psi_m\rangle\,. \tag{4}$$

In the context of core hole state calculation, the CVS approximation is employed to achieve such restriction.

2. *Block structure of the CVS Hamiltonian*

In order to highlight the principle of the CVS approximation, let us first distinguish between the different classes of Slater determinant that appear in the configuration interaction (CI) expansion of the wave function of a system. First, we consider the type of configurations that are preponderant in the CI expansion of SCH states, that is configurations with a single half-filled core orbital, these will be noted $|\mathrm{K}^{-1}\rangle$. Similarly, we will note by $|\mathrm{K}^{-2}\rangle$ configurations characterized by a single empty core orbital, these are the most important ones in the CI expansion of single site DCH states. We will use K' to signify any other core orbital than the one described by K, therefore $|\mathrm{K}^{-1}\mathrm{K}'^{-1}\rangle$ will represent a configurations with two vacancies on different core orbitals. Finally, we will depict by $|\mathrm{V}\rangle$ the "valence" configurations in which all the core orbitals are filled. To be as general as possible, the present definitions do not presuppose the charge of the system. Therefore, a $|\mathrm{K}^{-1}\rangle$ configuration may equally represent a neutral configuration obtained by a core excitation, or a cationic core hole configuration obtained by the removal of a core electron. We also note that these general notations are only made to focus on the occupation of core orbitals and do not imply anything about the occupation pattern of the valence/virtual MOs. Thus, a $|\mathrm{K}^{-1}\rangle$ configuration may also include valence to virtual excitations on top of the core excitation/ionisation (and similarly for DCH configurations).

One can show that the off-diagonal Hamiltonian matrix elements that couple a N-electron SCH Slater determinant with any other types of N-electron configuration can be neglected. Indeed, due to the highly local character of core orbitals, it comes that

$$\langle \mathrm{K}^{-1}|\hat{H}|\mathrm{K}'^{-1}\rangle \approx 0,\ \langle \mathrm{K}^{-1}|\hat{H}|\mathrm{K}'^{-2}\rangle \approx 0 \tag{5}$$

while configuration energy differences yield the following negligible perturbative weight :

$$\begin{aligned}&\frac{\langle \mathrm{K}^{-1}|\hat{H}|\mathrm{V}\rangle}{E^{\mathrm{K}^{-1}}-E^{\mathrm{V}}} \approx 0, \quad \frac{\langle \mathrm{K}^{-1}|\hat{H}|\mathrm{K}^{-2}\rangle}{E^{\mathrm{K}^{-1}}-E^{\mathrm{K}^{-2}}} \approx 0, \\ &\frac{\left\langle \mathrm{K}^{-1}\middle|\hat{H}\middle|\mathrm{K}^{-1}\mathrm{K}'^{-1}\right\rangle}{E^{\mathrm{K}^{-1}}-E^{\mathrm{K}^{-1}\mathrm{K}'^{-1}}} \approx 0,\ \frac{\left\langle \mathrm{K}^{-1}\middle|\hat{H}\middle|\mathrm{K}^{-1}\mathrm{K}'^{-2}\right\rangle}{E^{\mathrm{K}^{-1}}-E^{\mathrm{K}^{-1}\mathrm{K}'^{-2}}} \approx 0.\end{aligned} \tag{6}$$

Similar reasoning can be used for decoupling double core hole configurations from the others:

$$\begin{aligned}&\langle \mathrm{K}^{-2}|\hat{H}|\mathrm{K}^{-1}\mathrm{K}'^{-1}\rangle \approx 0,\ \langle \mathrm{K}^{-2}|\hat{H}|\mathrm{K}'^{-2}\rangle \approx 0,\\ &\langle \mathrm{K}^{-2}|\hat{H}|\mathrm{K}^{-1}\mathrm{K}'^{-2}\rangle \approx 0,\end{aligned} \tag{7}$$

and

$$\begin{aligned}&\frac{\langle \mathrm{K}^{-2}|\hat{H}|\mathrm{V}\rangle}{E^{\mathrm{K}^{-2}}-E^{\mathrm{V}}} \approx 0,\ \frac{\langle \mathrm{K}^{-2}|\hat{H}|\mathrm{K}^{-1}\rangle}{E^{\mathrm{K}^{-2}}-E^{\mathrm{K}^{-1}}} \approx 0, \\ &\frac{\left\langle \mathrm{K}^{-2}\middle|\hat{H}\middle|\mathrm{K}^{-2}\mathrm{K}'^{-1}\right\rangle}{E^{\mathrm{K}^{-2}}-E^{\mathrm{K}^{-2}\mathrm{K}'^{-1}}} \approx 0,\ \frac{\left\langle \mathrm{K}^{-2}\middle|\hat{H}\middle|\mathrm{K}^{-2}\mathrm{K}'^{-2}\right\rangle}{E^{\mathrm{K}^{-2}}-E^{\mathrm{K}^{-2}\mathrm{K}'^{-2}}} \approx 0.\end{aligned} \tag{8}$$

Numerical illustration of the approximate block-diagonal structure of the Hamiltonian is provided in figure 1 for the small BH^{2+} molecule. We consider this paradigm system whose small size allows exact computation of both full configuration interaction (FCI) and CVS eigenstates. The magnitude of the Hamiltonian coupling elements between two determinants labeled i and j is reported via the color grading. Said label were ordered according to the occupation of the Boron 1s orbital, first the core filed $|\mathrm{V}\rangle$ type determinants then the $|\mathrm{K}^{-1}\rangle$ ones and finally the $|\mathrm{K}^{-2}\rangle$. For ease of representation, the cc-pVDZ basis [49] was reduced by removing its component of "d" symmetry.

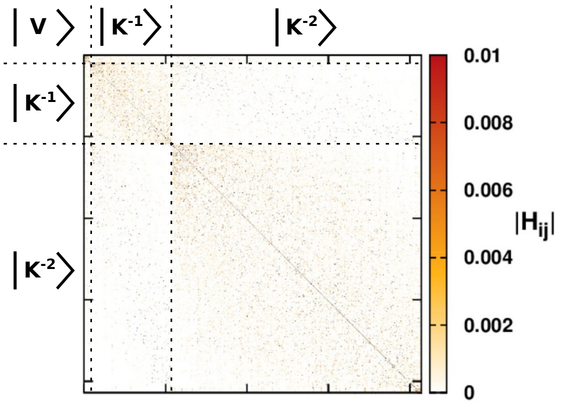

FIG. 1: Graphical representation of the Hamiltonian matrix of the BH^{2+} molecule computed for the VDZ′ basis (the cc-pVDZ basis without its "d" functions).

Neglecting these inter-block coupling terms yields the block-diagonal CVS Hamiltonian, $\hat{H}^{\mathrm{CVS}}$. Each of these block can thus be treated independently from the others to compute only states of the targeted SCH or DCH character.

We note that while the implementation of the CVS approximation within a CI strategy is fairly straightforward, other approaches such as the methods of the coupled cluster family leave more room to adjust the way in which this approximation is formulated (see e.g. [47]). As a result not all CVS implementations are strictly identical. However, as they are all built on the same central concept of separating the core hole states from the core filled ones, it is expected that they should retain a fairly similar overall behaviour.

3. *CVS approximation, CI expansion and variational principle*

The variational principle can now be restricted to applies only within a given block of the CVS Hamiltonian. Let us focus on the lowest single site DCH states for a given core orbital, $|\Psi_0^{\mathrm{K}-2}\rangle$, and its approximate CVS counterpart, $|\Psi_{\mathrm{CVS},0}^{\mathrm{K}-2}\rangle$. According to section II A 1, one can show that,

$$\begin{aligned}\left|\Psi_{\mathrm{CVS},0}^{\mathrm{K}-2}\right\rangle &= \arg\left(\min_{\varphi_{\mathrm{e}}\perp\{\overset{<}{\Psi}{}_{\mathrm{CVS},0}^{\mathrm{K}-2}\}}\left[\langle\varphi_{\mathrm{e}}|\hat{H}^{\mathrm{CVS}}|\varphi_{\mathrm{e}}\rangle\right]\right)\\ &= \arg\left(\min_{\varphi_{\mathrm{e}}\in\{\varphi^{\mathrm{K}-2}\}}\left[\langle\varphi_{\mathrm{e}}|\hat{H}|\varphi_{\mathrm{e}}\rangle\right]\right).\end{aligned} \tag{9}$$

This shows that the determination of $|\Psi_{\mathrm{CVS},0}^{\mathrm{K}-2}\rangle$ can be exactly reformulated as a ground state like calculation within a reduced variational space, $\{\varphi^{\mathrm{K}-2}\}$, comprised of wave-function whose CI expansion only contains configurations of the $|\mathrm{K}^{-2}\rangle$ type. This comes from the prevented mixing between $|\mathrm{K}^{-2}\rangle$ type determinants and the other ones due to the neglected inter-block coupling elements in the CVS Hamiltonian. This can be extended to "excited" DCH state by imposing orthogonality constraint in a standard fashion. Obviously, the previous development identically apply to SCH states and any other type of core hole state that can be isolated *via* the CVS approximation.

In equation (9), the orthogonality condition is defined with respect to the eigenstates of the CVS Hamiltonian. However, contrary to $\hat{H}^{\mathrm{CVS}}$, the true Hamiltonian still weakly couples the valence and (multiple) core hole configuration blocks, such that, all exact eigenstates will have some contribution of $|\mathrm{K}^{-2}\rangle$ determinants. Therefore, due to the imperfect nature of the CVS approximation, the relation in equation (4) is not exactly verified and any CVS states, $|\Psi_{\mathrm{CVS},n}^{\mathrm{K}-2}\rangle$, may display non-zero projection onto the $\{\overset{<}{\Psi}{}_n^{\mathrm{K}-2}\}$ set.

B. Limits of the CVS approximation

We now investigate the effects of the CVS approximation on double core hole states of the paradigm BH^{2+} system. We stress that the present calculations are not meant to accurately describe the DCH states of BH^{2+}, but to illustrate the spurious effects of the CVS approximation which are expected to be especially highlighted within this system due to the relative proximity between the different family of states isolated by this approximation. We used the cc-pVDZ and cc-pCVDZ basis sets [49, 50] in which we removed the functions of d symmetry to ease the computational burden. We label these basis VDZ′ and CVDZ′.

1. *CVS error on double core hole states energies*

In figure 2, we report the difference between the energy of the 50 lowest DCH states of BH^{2+} computed with and without applying the CVS approximation. Pairing between the CVS and FCI states was done using an overlap based procedure which consisted in projecting each CVS states on the FCI basis and associating them to the FCI state displaying the highest overlap value.

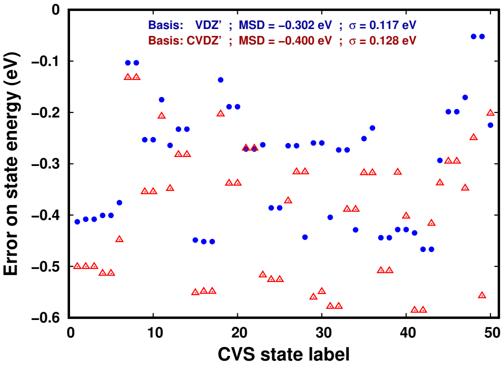

FIG. 2: Energy error due to the CVS approximation for the 50 lowest DCH states of BH^{2+} ($E_{\mathrm{CVS}} - E_{\mathrm{FCI}}$). Blue dots: VDZ′. Red triangles: CVDZ′.

One can clearly observe in figure 2 an underestimation of DCH states energies when the CVS approximation is applied. Indeed, when using the VDZ′ basis set, the energy of the $|\Psi^{\mathrm{K}-2}_{\mathrm{CVS},0}\rangle$ state was found about 0.4 eV below the FCI value, and about 0.5 eV with the CVDZ′ basis while over the 50 CVS states considered a mean signed deviation (MSD) of about -0.3 eV and -0.4 eV for the VDZ′ and CVDZ′ bases respectively. Such underestimation of the core hole state energy is expected to directly affect the determination of core excitation and binding energies since these are usually computed as difference between the energy of the system's ground state, free of CVS error, and the energy of the CVS core hole states. Moreover, as illustrated in the present case, the magnitude of the CVS error increases with the size of the basis set. This leads to the very unpleasant conclusion that when this error is dominant the quality of double core hole state computation strategy that relies on the CVS approximation is expected to deteriorate with the basis size.

In order to asses the generality of these observations, we shift our attention on the O 1s single site double core ionisation potentials (DCIP) of the CO and CO_2 molecules. We report in table I the values computed *via* different strategies based on the CVS approximation and with different basis sets. When a theoretical DCIP value was reported in the literature without taking into account relativistic effects we corrected it by a shift of 0.84 eV according to our estimation of this contribution obtained at the

TABLE I: CO and CO_2 O 1s DCIP (in eV) computed with a series of methods and basis sets. Bracketed values are the difference between the computed result and the best experimental estimate (respectively 1178.0 and 1174.35 eV; see ref. [51] and references therein). The (A)VXZ/(A)CVXZ nomenclature is used for Dunning's (aug-)cc-p(C)VXZ (X=D,T,Q,5) basis sets.

	CO (O K^{-2})	CO_2 (O K^{-2})
ΔCIPSI [10, 51]		
AVTZ	1177.87 (−0.13)	1174.06 (−0.29)
ACVTZ	1177.53 (−0.47)	1173.75 (−0.60)
ΔCIPSI (F. C.)$^{\mathbf{b}}$		
AVTZ	1177.51 (−0.49)	1173.67 (−0.68)
ACVTZ	1176.07 (−1.92)	1172.29 (−2.06)
ΔSCF [52, 53]		
VTZ	1176.22 (−1.78)	1173.66 (−0.69)
ACVTZ	1175.58 (−2.42)	1173.00 (−1.35)
ACVQZ	1175.16 (−2.84)	1172.59 (−1.76)
ACV5Z	1175.09 (−2.91)	1172.52 (−1.83)
ΔCASSCF$^{\mathbf{a,b}}$ [52]		
VTZ	1177.40 (−0.60)	1172.75 (−1.60)
CVTZ	1176.31 (−1.69)	-
VQZ	1176.21 (−1.79)	-
ΔCCSD$^{\mathbf{b}}$ [53]		
ACVTZ	1176.76 (−1.24)	1173.32 (−1.03)
ACVQZ	1176.07 (−1.93)	1172.65 (−1.70)
ACV5Z	1175.92 (−2.08)	1172.51 (−1.84)
ΔCCSD(T)$^{\mathbf{b}}$ [53]		
ACVTZ	1177.07 (−0.83)	1173.46 (−0.89)
ACVQZ	1176.38 (−1.62)	1172.80 (−1.55)
ACV5Z	1176.23 (−1.77)	1172.65 (−1.70)

[a] Active space comprising all occupied orbitals but the 1s and all the corresponding σ^* and π^* ones.
[b] Used the frozen core energy of the neutral state.

ΔCISD level using the third order Douglas Kroll transformation method (see refs. [10, 51]).

As one can see, all calculations reported here have predicted underestimated DCIP values. In most cases, these discrepancies cannot be directly attributed to the CVS error itself since other sources of error (typically the imperfect description of electronic correlation) still notably affect these results. In particular most results reported here were obtained using the frozen core energy of the neutral ground state thus participating to the underestimation of the DCIP as clearly illustrated by the two sets of selected CI (CIPSI) [48, 54–59] results. However, the CVS error is expected to be dominant in the case of the highly converged all electrons CIPSI calculations (top box of table I) for which more than 10^7 determinants were included in the CI space of both neutral and DCH states and also include a second order perturbative correction for the energy [10, 51]. Furthermore, one can also observe that all methods reported in table I show a clear increase in DCIP error with the size of the basis set. Standard correlation and basis set errors are not expected to explain such trend, especially in the cases of the usually very robust CCSD(T) and CIPSI based approaches. Therefore, these results provide indirect yet conclusive illustrations of the spurious effects of the CVS approximation on double core hole state energies, and of the unusual behaviour of the induced error with respect to the size of the basis set. Interestingly, for the present cases, the VTZ and AVTZ basis-sets without core correlation functions appear to be the best compromises between a good description of correlation effects and the control of the CVS error.

2. Interpretations of the CVS DCH state energy underestimation

Observing lower total energies for the CVS states than for their FCI counterpart might, at first, seems surprising. However, as discussed in section II A 3, the restriction imposed by the CVS approximation does not exactly enforce the orthogonality between the approximate CVS states and exact eigenstates of lower energy than the targeted core hole. Thus it follows that the energy of the exact core hole state is not a lower bound of the energy of the corresponding CVS state.

To asses the magnitude of such *contamination*, we report, in figure 3, the square value of the overlap between $|\Psi^{\mathrm{K}-2}_{\mathrm{CVS},0}\rangle$ and the 2500 lowest BH^{2+} FCI eigenstate computed with the VDZ′ basis.

Unsurprisingly, most of the projection of the $\Psi^{\mathrm{K}-2}_{\mathrm{CVS},0}$ wave function is concentrated on its FCI equivalent (approximately 99.9 %). However, one can also notice some non negligible projection onto very low lying SCH states. This observation explains why the energy of a CVS state falls below its exact FCI counterpart. Indeed, this shows that within the framework of the CVS approximation, the lack of a proper orthogonality constraint leads to the contamination of the CVS states by lower lying eigenstates with increased occupation number for their core orbital. Such states having significantly lower energy than the targeted core hole state, even a small contamination contributes to notably lower the energy of the CVS state.

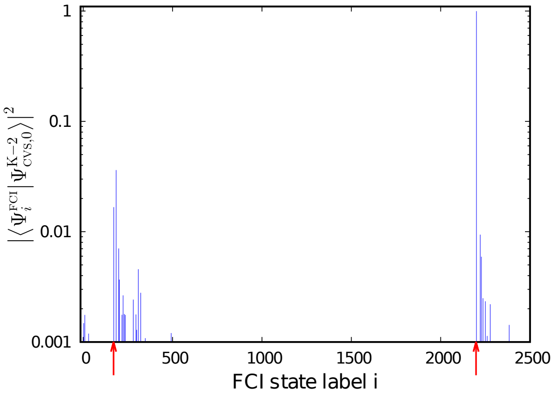

FIG. 3: Square value of the projection of the lowest energy DCH state of the BH^{2+} molecule computed within the CVS approximation onto the 2500 lowest eigenstate of the same system computed at the FCI level. The VDZ′ basis set was used. The two red arrows indicate the lowest SCH and DCH eigenstates.

Assuming the perfect validity of the CVS approximation implies that the exact FCI expansion of the DCH eigenstate would only have contribution from $|\mathrm{K}^{-2}\rangle$ type configurations. Interestingly, this gives us a way to assess the validity of the CVS approximation for our BH^{2+} test case. We report, in figure 4, the mean occupation number of the Boron 1s orbital in the 2500 lowest FCI states of the BH^{2+} system computed with the same two bases as previously considered.

As one can see, when the VDZ′ basis is employed, the system's behavior remains in line with what is expected when the CVS approximation is reasonable. Indeed, there is a clear separation between core filled states (mean occupation number of the Boron 1s orbital of 2), SCH states (mean occupation of 1), and DCH states (mean occupation of 0). However, increasing the flexibility of the basis by including orbitals designed to describe the correlation of core electrons leads to the blurring of this separation. Indeed, one can clearly observe that a large number of BH^{2+} eigenstates display mean occupation number of the Boron 1s orbital significantly away from an integer value when computed with the CVDZ′ basis. This clearly indicates that the validity of the CVS approximation decreases with the improvement of the basis set flexibility, especially in the core region.

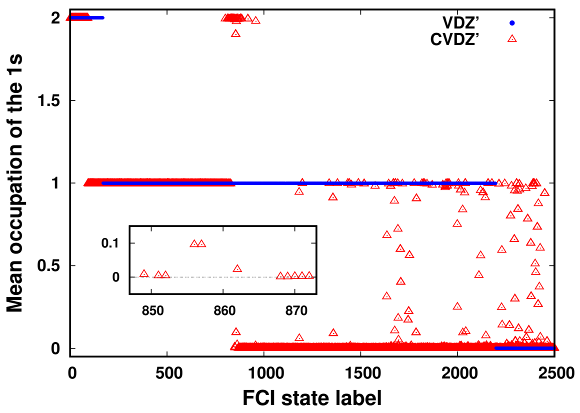

FIG. 4: Mean occupation number of the Boron 1s orbital in the 2500 lowest FCI states of BH^{2+}. Basis sets: VDZ′ (blue dots) and CVDZ′ (red triangles).

The two analysis that we conducted on the BH^{2+} CVS DCH states shed light on the intrinsic nature of the CVS approximation induced error and explain how it manifests in a calculation. First, we showed that the CVS constraint of only including in the CI space configuration with a given occupation number for the targeted core orbital is not equivalent to the exact orthogonality constraint appearing when properly applying the variational principle. As a result, this breach in the variational principle allows the CVS states to "leak" onto lower lying eigenstates with increased core occupation number. This spurious relaxation mechanism therefore yields CVS total energy that are underestimated with respect to the exact FCI values. We then illustrated that the validity of the CVS approximation is notably modulated by the nature of the basis set used. In particular, we highlighted that improving the flexibility of the basis in the core region leads to a decrease in the validity of the CVS approximation thus explaining the rise in the CVS error with the size of the basis.

3. *Comparison with the case of SCH calculation*

We now confront our finding regarding the effects of the CVS approximation on DCH states with some of the known properties of the CVS error in the context of SCH states calculation. The critical difference that exists between the CVS approximation as applied for computing SCH states in comparison with DCH ones is the nature of the discarded configurations.

According to equations (5) and (6), when targeting SCH states, the CI expansions of the wave functions are striped of (i) all valence type configurations, (ii) all single site double core hole involving the core orbital bearing the core vacancy in the targeted states, and (iii) all configuration involving core vacancies located on other core orbitals. Generally speaking, neglecting the mixing between core hole states localised on different atoms should remain a fairly good approximation in most cases, which leaves us to asses the effects of the missing $|V\rangle$ and $|\mathrm{K}^{-2}\rangle$ configurations. From a perturbative point of view, $|\mathrm{K}^{-2}\rangle$ configurations are expected to lower the SCH state energy while $|V\rangle$ determinants should lead to its increase. The CVS error in SCH calculation is thus expected to stem from the balance between two components of opposite effects. This reasoning has been previously used by Herbst *et al.* to investigate the CVS error in the context of SCH calculations using the ADC method [37]. This explains why the CVS error have been observed to yield both positive and negative shift of the energy of SCH states.

This strongly contrasts with the CVS error in single site DCH states calculations. Indeed, in the latter, the CVS error mostly stems from the missing $|V\rangle$ and $|\mathrm{K}^{-1}\rangle$ configurations (once again leaving aside the effects of core hole mixing configurations). Contrary to the SCH case, all missing Slater determinants are expected to increase the energy of the DCH states. This observation is in adequacy with our previous observation of a CVS error leading to a significant underestimation of the single site DCH states' energies. Moreover, the lack of error compensation between the two main components of the CVS error leads to the conclusion that the spurious effects of the CVS approximation should be significantly more marked in the case of DCH states than SCH ones.

As a final remark, we note that by using the same reasoning, one can conclude that the CVS error associated with the computation of two site DCH states should behave more similarly to the SCH case than to the single site DCH one. This intuition is confirmed by the observations of Zheng *et al.* who reported positive energy shifts of a series of two site DCH states as a result of the CVS approximation [43].

III. CORRECTION OF THE CVS ERROR

A. Short overview of existing procedures

The CVS approximation being a critical aspect of core hole state computation methods, attempts had already been made to asses and correct its spurious effects. As, the CVS approximation can be seen from multiple points of view and summarizing its consequences is not trivial, the correction strategies that have been proposed so far were based on very different ideas.

Zheng *et al.* devised an *ad hoc* correction strategy in which they assimilate the CVS error to a global energy shift of the CVS states [42, 43]. They evaluated this shift as the difference between the core hole state energy obtained in a CVS-CCSD(T) calculation and a non CVS one. Obviously, this suppose that the core hole states can be properly computed within the non-CVS coupled cluster calculation. In their study, this was made possible by applying very drastic restrictions on the excitations included in the calculation.

As it was explained previously, applying the CVS approximation leads to leaving a large number of configurations out of the variational space explored. Therefore, one may choose to deal with the CVS error by focusing on that discarded information. A natural way of accounting for that is to use perturbation theory. This idea was explored by Coriani *et al.* in the context of coupled cluster calculations, [41] as well as Garner *et al.* for excited state mean field calculations [46].

One may instead attempt to directly correct the CVS core hole wave functions. In that approach, the focus is put on the CVS internal space rather than on its external complementary part as for the perturbative approach. This strategy was adopted by Herbst *et al.* who proposed to use a state specific Rayleigh-quotient iteration procedure to relax *a posteriori* the CVS state. This strategy is based on the idea that a CVS state energy is a good enough guess to allow the convergence of the non variational procedure. One important distinction between this approach and the previous ones is that it allows to correct both the CVS energies and wave functions. Thus, it could also be used to correct transition properties.

So far, such correction schemes have mostly been used in the case of SCH calculations. It is still to be noted that, as stated before, Zheng *et al.* applied their *ad hoc* strategy to a series of two site double core hole states. However, when targeting DCH states rather than lower lying SCH ones, very strict restrictions need to be applied to the CVS approximation-free calculation thus significantly limiting the practicability of such approaches. On the other hand, owing to its state specific nature, the Rayleigh-quotient iteration based procedure of Herbst *et al.* should not suffer from the extension to DCH states since its only premise is that the energies of the CVS states are good enough. However, as it was shown in figure 2, the CVS error cannot be reduced to a simple shift on the core binding energy but instead, affects the different core hole states with a varying magnitude. Thus, when using a state specific strategy, each states will need to be independently corrected which could then lead to interpretation problem since independent Rayleigh-quotient iteration procedure might not yield properly orthogonal core hole states. Finally, the perturbative correction strategy can be straightforwardly extended to CI based calculation of DCH states. As highlighted before, this perturbative correction would indeed yield a positive shift of the energies of the BH^{2+} DCH states since the $|V\rangle$ and $|K^{-1}\rangle$ determinants are expected to mostly be of significantly lower energies that the CVS DCH states.

B. A variational correction of the CVS error

1. An energy maximization strategy

In the following, we design a variational procedure that allows to correct, in a coherent manner, a series of CVS core hole states. To do so, we propose to diagonalize the Hamiltonian operator in a basis built with (*i*) the set of contracted CVS core hole wave function to be corrected, and (*ii*) a selected part of the set of external determinants discarded within the CVS approximation.

This idea will be applied to correct the CVS error in the DCH state of the BH^{2+} system that we investigated before. In practice, the corrected wave functions will now be expanded as:

$$\left|\bar{\Psi}_n\right\rangle = \sum_m C_m^n \left|\Psi_{\text{CVS},m}^{\text{K}-2}\right\rangle + \sum_i P_i^n \left|\Phi_i^{\text{ext.}}\right\rangle, \quad (10)$$

where $\{\Phi^{\text{ext.}}\}$ is the set of external determinants not included in the CVS CI space. The identification of the corrected roots corresponding to the targeted DCH state, $|\bar{\Psi}_n^{\text{K}-2}\rangle$, only involves finding those whose expansion is dominated by a very large C_m^n coefficient.

Through this approach, the CVS error is corrected in two ways. First, taking into account the external determinants $\{\Phi^{\text{ext.}}\}$ corrects a similar aspect of the CVS error than the strategies based on perturbation theory. However, in this approach, these determinants are explicitly included into the corrected wave functions. A global correction of any observable is therefore expected rather than just an energy shift. On top of that, within our variational approach, a small mixing between the contracted CVS wave functions is expected due to indirect coupling *via* the determinants of the external space. As a result, this approach also allows for the partial relaxation of the CVS approximation within the internal CVS determinant space, akin to what can be achieved using Herbst *et al.*'s Rayleigh-quotient procedure. However, we highlight that within our method, all CVS states are corrected simultaneously and the orthogonality of the !corrected roots is ensured.

For this strategy to be applicable in practice, one would need to be able to reliably compute the corrected core hole wave functions. Let us first note that including the full set of CVS wave functions and the full set of external determinants in equation (10) would restore the complete FCI flexibility

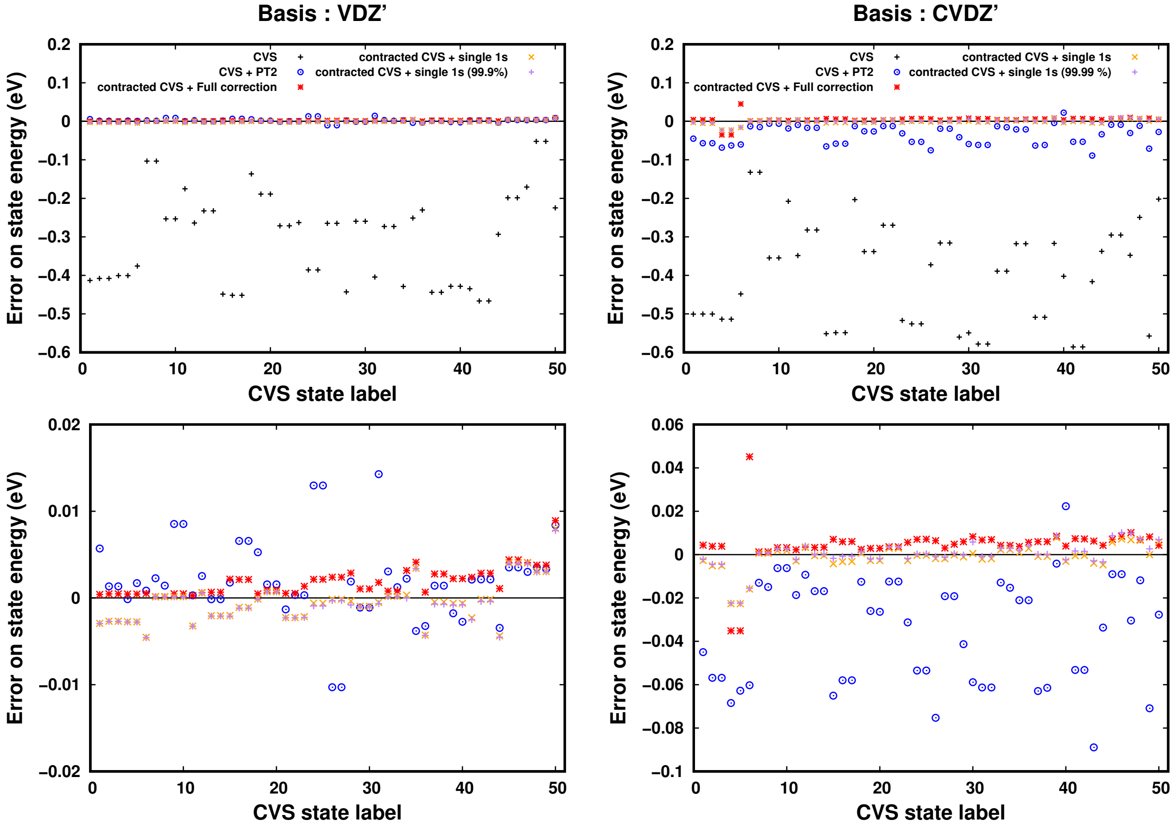

FIG. 5: Error on the energy ($E - E_{\mathrm{FCI}}$) of the 50 lowest DCH state of BH^{2+} computed within the CVS approximation and with a series of correction (see text). Left: VDZ′ basis-set. Right: CVDZ′ basis-set. The two bottom panels show a zoom on the 0 eV error region.

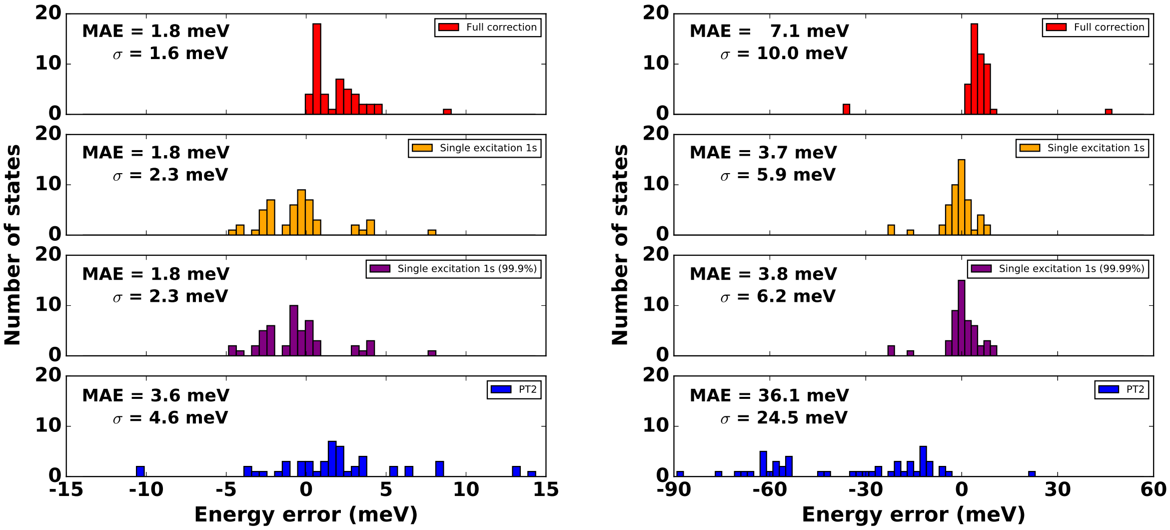

FIG. 6: Histogram of the distribution in residual energy error ($E - E_{\mathrm{FCI}}$) for the 50 lowest DCH state of BH^{2+} after correction of the CVS error using the same methods as in Fig. 5. Left: VDZ′ basis-set. Right: CVDZ′ basis-set. We also report the mean absolute error (MAE) and standard deviation for each method. We recall that for the uncorrected CVS calculations, MSD = -302.5 meV and $\sigma = 116.9$ meV with the VDZ′ basis set and MSD = -400.1 meV and $\sigma = 128.2$ meV with the CVDZ′ basis set (see Fig. 2). We used the MSD values here since the uncorrected CVS error is fully negative.

and thus yields the exact eigenstates of the electronic Hamiltonian. Obviously, in practice, both of these sets have to be truncated. Generally speaking, the set of CVS states to be corrected will be naturally small since it will only contain the CVS core hole states initially computed. However, even with that restriction, one still encounter an issue similar to the one that leads to the use of the CVS approximation in the first place. Indeed, the corrected core hole states are, once again, expected to be found somewhere in the middle of the spectrum of the electronic Hamiltonian.

To circumvent this problem, we propose to restrict the external determinant set such that the core hole roots lie strictly at the top of the eigenvalue spectrum of the electronic Hamiltonian projected onto the correction basis. To do so, we only include in $\{\Phi^{\text{ext.}}\}$, Slater determinants of energy significantly lower than the CVS states. As a result, no root that favor P_i^n coefficients will be of higher energy than the roots dominated by the contracted CVS states *i.e.* the one mostly weighted by a C_m^n coefficient. Within this framework, one can easily compute these roots in an almost standard variational way. Indeed, to target the higher edge of the eigenvalue spectrum, one can consider the opposite electronic Hamiltonian $(-1 \times \hat{H})$ and use a standard Davidson procedure to compute the lowest energy edge of this modified operator.

2. Results for the 50 lowest DCH states of BH^{2+}

We applied our corrections procedures on the 50 lowest CVS DCH states of the BH^{2+} molecule for which the CVS error was characterized in figure 2. To truncate the external determinant space, we rely on the observations made in section II B 3 and using figure 3. We highlighted that, for these DCH states, a major origin of the CVS error is the contamination of the CVS states by low energy SCH ones. We thus propose to include in the external determinant set, only $|\text{K}^{-1}\rangle$ type configurations that can be generated as a single valence-to-core excitation from a $|\text{K}^{-2}\rangle$ Slater determinant included in the initial CVS CI space.

We report in figure 5 the error with respect to the FCI on the energy of the 50 lowest energy DCH states of BH^{2+} computed within the CVS approximation (black) and after applying our variational correction with (*i*) the full set of external determinants (red), (*ii*) the restricted set of external determinants generated as valence-to-core single excitation from all configurations in the CVS CI space (orange), and (*iii*) the restricted set of external configuration generated from the determinants that span at least 99.9% (VDZ′) and 99.99% (CVDZ′) of the norm of each CVS wave functions (purple). This latter restriction was enforced by sorting the CVS CI space configurations according to their state average weight and picking the smallest most relevant portion such that the accounted norm is greater than the requested threshold for each CVS state. In the present cases this lead to a division by 2 of the number of determinants in the correction space. We also report the results obtained with the perturbative correction arising from the full set of external determinants (blue). Here we used second order Epstein-Nesbeth perturbation theory such that

$$E_n^{\text{PT2}} = E_n^{\text{CVS}} + \sum_i \frac{|\,\langle \Psi^{\text{K}-2}_{\text{CVS},n}|\hat{H}|\Phi_i^{\text{ext.}}\rangle\,|^2}{E_n^{\text{CVS}} - \langle \Phi_i^{\text{ext.}}|\hat{H}|\Phi_i^{\text{ext.}}\rangle}. \quad (11)$$

Finally, we report in figure 6 a series of histograms showing the residual energy error distributions after applying the CVS corrections previously mentioned. The mean absolute error (MAE) and standard deviation (σ) are also given for each correction methods.

These figures show a clear improvement in DCH state energies after correcting the CVS error with any of the method considered here. Interestingly, our variational correction yields very similar results whether the full set of external determinants is taken into account or if it is restricted to valence-to-core single excitation only. We stress again that only the procedure in which the external determinant set is generated by single excitation would be applicable in a real life scenario since including the full set of external determinants would not allow for the variational computation of the double core hole roots. In the present case, the results for the complete correction set were obtained by fully diagonalizing the electronic Hamiltonian projected on the correction basis. One can also observe that almost identical results are obtained whether the restricted set of external determinants was generated from all the configurations in the CVS CI space or only from configurations that span 99.9% (VDZ′) and 99.99% (CVDZ′) of the norm of the CVS wave functions. This drastically reduces the size of the external set thus allowing the generalization of this method to larger systems.

One can notice that, for few states, when the CVDZ′ basis set is used, the variational correction obtained with the restricted set of external determinants yields more accurate results than the correction obtained with the full set of external determinants. In particular, this is the cases for the fourth, fifth, and sixth DCH states as it can be clearly seen in the bottom right panel of figure 5. Interestingly, the initial CVS approximation may already have been especially less adequate for these three specific DCH states. Indeed, figure 4 shows that the expected core occupation for these three DCH states notably differs from 0. This means that some configurations with at least one electron in the core orbital are expected to be relatively important in the exact description of these states. In our variational correction method, the relaxation of the contracted CVS wave-functions is only partially allowed, therefore it is not surprising to observe some instability when external determinants bearing large coefficients are included.

If both perturbative and variational corrections significantly mitigate the CVS error, clear differences between these procedures can be observed on the bottom panels of figure 5. Notably, one can see that the residual error is significantly larger when applying the perturbative correction than with our variational strategy. Similarly, the residual error spread is largely reduced with the variational approach in regard to the perturbative one as clearly illustrated by figure 6.

Interestingly, the reliability of the variational correction seems to be less dependent on the basis set than the perturbative one. Indeed, the mean average error observed after application of the perturbative correction increases by an order of magnitude when going from the VDZ′ to the CVDZ′ basis set while the residual mean average error obtained after application of our variational correction procedure (with the external determinant set built by single excitation) only increases by a factor two. Moreover, the standard deviation of the error after perturbative correction increases by more than a factor five between the two basis while it increases by less than a factor three with the variational correction. Typically, the accuracy of truncated CI approaches with respect to perturbative ones tends to deteriorate with the size of the system due to the increases in size consistence error which grows with the amount of correlation and relaxation energy. However, in the cases of core hole state, the highly local nature of the relaxation due to the local hole created should not lead to size consistence error that scales linearly with the size of the system. Therefore, it is expected that the present procedure will not display a constant increase in the error with the system size.

IV. CONCLUSION

We investigated the spurious effects of the CVS approximation, especially in the context of double core hole state calculations. By performing exact FCI calculations on the model system BH^{2+}, we showed that the CVS approximation induces a breach in the variational principle due to the loss of exact orthogonality conditions leading to the systematic underestimation of the energy of double core hole states. Indeed, we illustrated that the CVS approximation results in the contamination of DCH states by lower lying SCH ones, and thus, to CVS states of too low energies. We also highlighted that this error increases with the size of the basis set, especially when core correlation functions are added. This interpretation is shown to be in adequacy with theoretical results displaying a systematic underestimation of the double core ionisation potential of the CO and CO_2 molecules, and explains the different behavior of the CVS error in the case of SCH calculations.

We also developed a variational method for correcting the CVS error which was designed to simultaneously correct a series of CVS states while preserving the orthogonality of the corrected wave functions. This approach is based on the idea of projecting the electronic Hamiltonian onto a basis containing the contracted CVS core hole wave functions to be corrected as well as relevant Slater determinants discarded due to the CVS approximation. In practice, we proposed to build this basis such that the targeted core hole roots are found at the higher edge of the Hamiltonian eigenvalue spectrum. The corrected core hole wave functions can then be variationally computed *via* an energy maximization procedure. We showed that for the DCH states of BH^{2+}, this method yields results of higher quality than a perturbative strategy.

Through this paper, we focused on unraveling the specificities of the CVS error in the context of double core hole calculations, and on presenting a proof of principle for our variational correction strategy. In upcoming works, we plan on be generalizing this method to be applicable to *real life* cases. Since the formalism presented here can be trivially generalized to any CI / selected CI based calculations, our short term focus will be on the correction of the CVS error in the double core hole states of the CO and CO_2 dications previously investigated by some of the present authors [10, 51]. We also plan on assessing the effects of the CVS error on non energetic properties such as theoretical excitation/ionization transition moments.

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Data Availability

The data that supports the findings of this study are available either within the text, the referenced articles, or from the corresponding authors upon reasonable request.

Conflicts of interest

There are no conflicts of any sort to declare.

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