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Communication: An inexpensive, variational, almost black-box, almost size-consistent correction to configuration interaction singles for valence excited states

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Configuration interaction singles (CIS) describe excited electronic states only qualitatively and improvements are imperative as a means of recovering chemical accuracy. In particular, variational improvements would be ideal to account for state crossings and electronic relaxation. To accomplish such an objective, in this communication we present a new suite of algorithms, abbreviated VOO-CIS for variationally orbital optimized CIS. We show below that VOO-CIS yields a uniform improvement to CIS, rebalancing the energies of CT states versus non-CT states within the same framework. Furthermore, VOO-CIS finds energetic corrections for CT states that are even larger than those predicted by CIS(D). The computational cost of VOO-CIS depends strongly on the number of excited states requested (n), but otherwise should be proportional to the cost of CIS itself.

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I. INTRODUCTION

CIS Inspired Approaches. Configuration interaction singles (CIS) is a size-consistent, variational approach positing that an excited state wavefunction (labeled I) is a linear combination of single excitations: $|\Psi_{\text{CIS}}^I\rangle = \sum_{ai} t_i^{aI} |\Phi_i^a\rangle$. The amplitudes $\{t_i^{aI}\}$ are found by diagonalizing the resulting Hamiltonian.

When excited states have “similar character”—so that their correlation energies cancel—CIS can predict relative excitation energies reasonably well.¹ However, when excited states have different character, CIS performs poorly and the ordering of the excited states is completely unreliable. In particular, CIS fails miserably when it comes to the relative energies of non-CT and CT states, consistently overestimating CT energies by roughly 1–2 eV.²

To improve upon CIS with wavefunctions, CIS(D)³ is a good approach, introducing electron correlation by including perturbations from all doubles and a subset of the triples. (Another option is CIS(2).⁴) CIS(D) almost always outperforms CIS, sometimes reducing the excitation energy errors to a few tenths of an eV.⁵ However, because CIS(D) is perturbative, the biggest limitation of the method is that one cannot handle crossings or near-degeneracies accurately. Thus, CIS(D) does not yield reliable excited states in the regions most important to electronic relaxation and analytical gradients are not available. Finally, there is a quasi-degenerate improvement to CIS(D), CIS(D)₀,⁶ but the latter is quite expensive and requires the iterative diagonalization of a perturbative response matrix (without being variational); recent progress has focused on the scaled-opposite-spin (SOS-CIS(D)₀) approximation and gradient.^{7,8}

Orbital Optimization for Charge-Transfer States. CT states are ubiquitous in excited state chemistry. From our point of view, $n \rightarrow \pi^*$ states count as CT states in small organics, given that the donor lone pair (n) usually belongs to an oxygen, and the acceptor π^* orbital can be one or two bonds away on carbon atoms. If we want to use wavefunction methods for excited states, the CIS imbalance between CT and non-CT states must be corrected.

In a recent paper, we showed that the CT problem in CIS can be effectively overcome by simple orbital optimization.⁹ In fact, we demonstrated that a perturbative approach for reoptimizing orbitals (which we called OO-CIS)⁹ yielded a large negative energy correction for CT states which was comparable to CIS(D). Nevertheless perturbation theory is never suitable near a crossing point. Moreover, we have found empirically that OO-CIS (even more so than CIS(D)) does not give a big enough correction to CT states.¹⁰

To go beyond our earlier perturbative approach, we now present a new and variational extension of OO-CIS, labeled VOO-CIS, rooted in the concept of orbital optimization. VOO-CIS predicts accurate relative energies between CT states and non-CT ones, and because the latter is variational, it can effectively address the electronic structure problem at a crossing point.

Notation. Henceforward, $ijkl$ ($abcd$) denote occupied (virtual) orbitals. $IJKL$ are the indices for excited states, while G is reserved for ground state. $\tilde{I}\tilde{J}\tilde{K}\tilde{L}$ are indices for either a ground or excited state. When we write VOO-CIS- $C(n, m)$, n denotes the number of excited CIS states included and must be less than or equal to the size of the CIS-subspace N_{ov} . m is an indication of how many doubles are involved in the basis wavefunctions and can only be $\{1, 2, 3\}$, i.e., the number of doubles from excited states is n^m . C can be any of the three characters $\{O, G, X\}$. See Table I for detailed meaning of m and C .

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TABLE I. For each VOO-CIS-C(n, m) option, here are the additional subspaces included along with the CIS states $\{|\Psi_{\text{CIS}}^I\rangle\}$. $I, J, K, L = \{1, 2 \dots n\}$.

m	C		
	O ^a	G	X
1	$ \Psi^{JJJ}\rangle$	$ \Phi_{\text{HF}}\rangle, \Psi^{JJJ}\rangle$	$ \Phi_{\text{HF}}\rangle, \Psi^{JJJ}\rangle$
2	$ \Psi^{JKK}\rangle$	$ \Phi_{\text{HF}}\rangle, \Psi^{JKK}\rangle$	$ \Phi_{\text{HF}}\rangle, \Psi^{JKK}\rangle, \Psi^{GKK}\rangle$
3	$ \Psi^{JKL}\rangle$	$ \Phi_{\text{HF}}\rangle, \Psi^{JKL}\rangle$	$ \Phi_{\text{HF}}\rangle, \Psi^{JKL}\rangle, \Psi^{GKL}\rangle$

^aStrictly speaking, only the O-option is size-consistent.

II. METHODOLOGY: DOUBLES CORRECTIONS VIA ORBITAL RELAXATION

Basis. The basic premise of VOO-CIS is to treat a set of CIS wavefunctions $|\Psi_{\text{CIS}}^I\rangle$ as zeroth order wavefunctions $|\Psi^{(0)}\rangle$. Next, we generate first order wavefunction corrections $|\Psi^{(1)}\rangle$ by projecting the effect of orbital optimization onto the space of double excitations. Finally, we rediagonalize the entire Hamiltonian in the basis $\{|\Psi^{(0)}\rangle, |\Psi^{(1)}\rangle\}$.

With this in mind, we are led to the following doubly excited configurations, where the ground-state $|\Phi_{\text{HF}}\rangle$ can either be included or not,

$$\begin{aligned}
 |\Psi^{JKL}\rangle &= - \sum_{ai} \frac{\langle \Psi_{\text{CIS}}^J | H | a_a^\dagger a_i \Psi_{\text{CIS}}^K \rangle}{\epsilon_a - \epsilon_i + E_{\text{CIS}}^K - E_{\text{CIS}}^J} a_a^\dagger a_i |\Psi_{\text{CIS}}^L\rangle \\
 &\equiv - \sum_{ai} \frac{Y_{ai}^{JK}}{\epsilon_a - \epsilon_i + E_{\text{CIS}}^K - E_{\text{CIS}}^J} a_a^\dagger a_i |\Psi_{\text{CIS}}^L\rangle \\
 &\equiv + \sum_{ai} \theta_{ai}^{JK} a_a^\dagger a_i |\Psi_{\text{CIS}}^L\rangle, \quad (1)
 \end{aligned}$$

$$\begin{aligned}
 |\Psi^{GKL}\rangle &= - \sum_{ai} \frac{\langle \Phi_{\text{HF}} | H | a_a^\dagger a_i \Psi_{\text{CIS}}^K \rangle}{\epsilon_a - \epsilon_i + E_{\text{CIS}}^K - E_{\text{HF}}} a_a^\dagger a_i |\Psi_{\text{CIS}}^L\rangle \\
 &\equiv - \sum_{ai} \frac{Y_{ai}^{GK}}{\epsilon_a - \epsilon_i + E_{\text{CIS}}^K - E_{\text{HF}}} a_a^\dagger a_i |\Psi_{\text{CIS}}^L\rangle \\
 &\equiv + \sum_{ai} \theta_{ai}^{GK} a_a^\dagger a_i |\Psi_{\text{CIS}}^L\rangle. \quad (2)
 \end{aligned}$$

Here, in the basis of molecular orbitals, the Y and θ matrices are

$$\begin{aligned}
 Y_{ai}^{IJ} &\equiv \sum_{bcjk} t_k^{cI} \langle \Phi_k^c | H | a_a^\dagger a_i | \Phi_j^b \rangle t_j^{bJ} \\
 &= \sum_{bcj} (t_i^{cI} t_j^{bJ} \langle cj || ab \rangle + t_j^{cI} t_i^{bJ} \langle ci || ba \rangle) \\
 &\quad + \sum_{bjk} (t_k^{aI} t_j^{bJ} \langle ij || bk \rangle + t_k^{bI} t_j^{aJ} \langle ij || ka \rangle), \quad (3) \\
 Y_{ai}^{GJ} &\equiv \sum_{bj} \langle \Phi_{\text{HF}} | H | a_a^\dagger a_i | \Phi_j^b \rangle t_j^{bJ} = \sum_{bj} t_j^{bJ} \langle ij || ab \rangle, \\
 \theta_{ai}^{\tilde{I}J} &\equiv - \frac{Y_{ai}^{\tilde{I}J}}{\epsilon_a - \epsilon_i + E^J - E^{\tilde{I}}}.
 \end{aligned}$$

The VOO-CIS algorithm proposes that we pick a subset of the $\{|\Psi^{JKL}\rangle\}$ vectors listed above (Eqs. (1) and (2))

as $|\Psi^{(1)}\rangle$. Broadly speaking, we have three major choices for subspace size: ($m = 1$) corresponds to state specific orbital optimization by first-order perturbation theory: $|\Psi_{\text{CIS}}^I\rangle \rightarrow |\Psi_{\text{CIS}}^I\rangle + c^{III} |\Psi^{III}\rangle$. ($m = 2$) corresponds to both intrastate and interstate orbital relaxation: $|\Psi_{\text{CIS}}^I\rangle \rightarrow |\Psi_{\text{CIS}}^I\rangle + \sum_J c^{IJJ} |\Psi^{IJJ}\rangle$. ($m = 3$) corresponds to $|\Psi_{\text{CIS}}^I\rangle \rightarrow |\Psi_{\text{CIS}}^I\rangle + \sum_{JK} c^{IJK} |\Psi^{IJK}\rangle$, which is unphysical but does ensure stability at a point of conical intersection between CIS states. Finally, before finishing, we must almost decide whether or not to include the ground state, and if so how. In Table I, we list all the possible choices of the basis set.

Hamiltonian. Our next task is to construct the Hamiltonian H matrix. Notice that the maximum dimension is $D = 1 + n + n^3 + n^2$, where 1 is the ground state and n is the number of excited states we desire. More specifically, n is the dimension for the $|\Psi^{(0)}\rangle$ vector space, while n^3 and n^2 are, respectively, the dimensions for the $\{|\Psi^{JKL}\rangle\}$ and $\{|\Psi^{GKL}\rangle\}$ subspaces of the $|\Psi^{(1)}\rangle$ vector space.

The H matrix is naturally divided into 3 parts:

$$\begin{aligned}
 \langle \Psi^{\tilde{I}} | H | \Psi^{\tilde{J}} \rangle &= \delta_{\tilde{I}\tilde{J}} E^{\tilde{I}}, \\
 \langle \Psi^{\tilde{I}} | H | \Psi^{\tilde{J}KL} \rangle &= \sum_{ai} \langle \Psi^{\tilde{I}} | H | \theta_{ai}^{\tilde{J}K} a_a^\dagger a_i \Psi^L \rangle \\
 &= \sum_{ai} \theta_{ai}^{\tilde{J}K} Y_{ai}^{\tilde{I}L}, \quad (4) \\
 \langle \Psi^{\tilde{I}JK} | H | \Psi^{\tilde{I}'J'K'} \rangle &= \sum_{abij} \langle (\Psi^K \theta_{bj}^{\tilde{I}J} a_j^\dagger a_b) | H | (\theta_{ai}^{\tilde{I}'J'} a_a^\dagger a_i \Psi^{K'}) \rangle \\
 &= \sum_{abij} \theta_{bj}^{\tilde{I}J} \theta_{ai}^{\tilde{I}'J'} \langle \Psi^K | a_j^\dagger a_b H a_a^\dagger a_i | \Psi^{K'} \rangle.
 \end{aligned}$$

The last matrix element is easily evaluated via second-quantization.

Because our basis functions are neither normalized nor orthogonal, we must diagonalize the H matrix together with the overlap S matrix: $Hv = SvE$. Basis functions used in the doubles space can be linearly dependent, so when diagonalizing the S matrix, we use a threshold of 10^{-5} for eigenvalues to eliminate linear dependence. In practice, if we choose $n = 10$ excited states, we need to diagonalize a matrix at most (when $m = 3$) on the order of 1000 by 1000.

Finally, note that the eigenfunctions of the Hamiltonian in Eq. (4) will not couple together non-interacting subsystems, provided the ground state is not included. Thus, the VOO-CIS-O option is completely size-consistent.

III. RESULTS

The VOO-CIS algorithm was implemented using a developers' version of the Q-Chem software package.¹¹ In the following calculations, the basis set was 6-31G* together with the rimp2-cc-pvdz auxiliary basis set. We present results for two molecules: 2-(4-(propan-2-ylidene)cyclohexylidene)malononitril (PYCM, shown in the inset of Fig. 1(f)) and twisted ethylene (C_2H_4).

PYCM. Experimentally, the absorption spectrum of PYCM shows a strong non-CT band at 5.4 eV and a CT

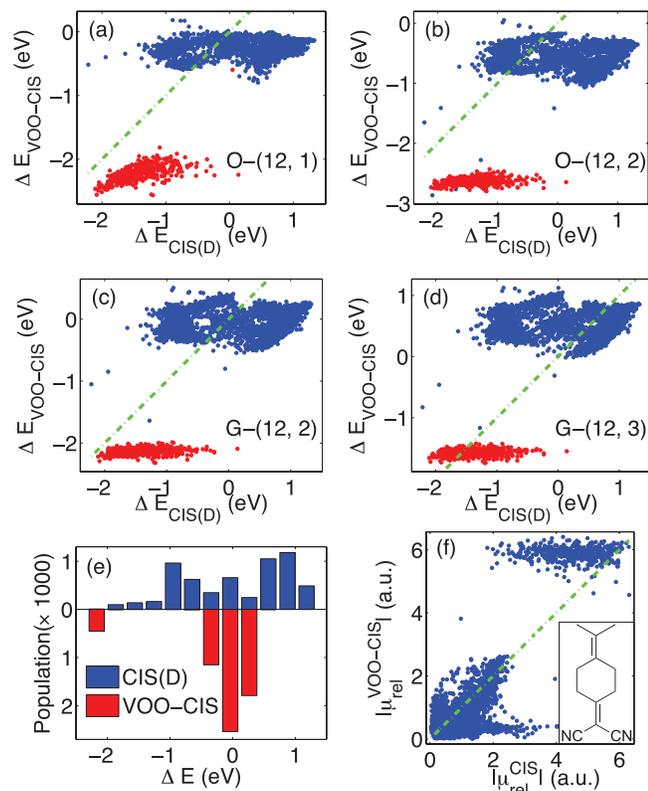


FIG. 1. (a)–(d) Plot of the VOO-CIS energy correction versus the CIS(D) energy correction, with different VOO-CIS options for m and C . Data points with $|\vec{\mu}_{\text{rel}}|$ bigger than 4 a.u. are colored red (for CT states); non-CT states are colored blue. (e) A histogram of energy corrections from both CIS(D) and VOO-CIS-G(12, 2). (f) Plot of the VOO-CIS-G(12, 2) $|\vec{\mu}_{\text{rel}}|$ versus $|\vec{\mu}_{\text{rel}}^{\text{CIS}}|$. The inset is the PYCM structure. All the green lines are $y = x$ for reference. Note that all VOO-CIS combinations find a clear separation between CT and non-CT states, while CIS(D) does not.

band at 4.6 eV in hexane.¹² At the ground-state geometry, CIS incorrectly predicts that the CT state is the 7th state, while CIS(D) correctly predicts the CT state is the first excited state. Surprisingly (and incorrectly), SOS-CIS(D₀)⁷ finds two (mixed) low-lying excited states with large dipole moments.

In this communication, we will focus exclusively on the potential energy surface near the ground-state geometry. Previously,² we have generated 500 geometries from a ground-state classical trajectory, and we consider the first 12 excited states, each with roughly 1 CT state apiece, for a total of 6000 data points. In this region of configuration space, with no torsional motion, we do not expect to see any crossings between the CT and non-CT state.¹³ Strangely, however, CIS does predict such crossings. When faced with such an unexpected crossing, CIS(D) encounters adiabatic CIS states that are incorrectly mixtures of CT and non-CT states; as such, CIS(D) is forced to give a correction lying anywhere from big to small. As such, according to CIS(D), the CT state is not consistently the lowest excited state.

By contrast, VOO-CIS does not predict such a crossing. In Figs. 1(a)–1(d), we plot the VOO-CIS energy correction versus CIS(D) energy correction for different combinations of parameters in VOO-CIS-C(n , m). The red dots are from CT states, while blue dots are from non-CT ones. To construct $\Delta E_{\text{VOO-CIS}}$, we mapped each CIS eigenstate to the VOO-CIS

eigenstate with maximum overlap. The data are striking: unlike CIS(D), VOO-CIS always finds a sharp boundary for ΔE between non-CT and CT states and does not mix CT and non-CT states. The $m = 2$ and $m = 3$ corrections give an even more consistent correction than $m = 1$. (By comparing Figs. 1(c) with 1(b), we see that adding in the ground-state can shift all the excitation energies up.) Our data is summarized in Fig. 1(e) which shows a histogram of energy corrections for CIS(D) and VOO-CIS-G(12, 2). The former has a wide and continuous distribution, while the latter yields a bimodal distribution – with one sharp peak for CT states (≈ -2 eV) and another for non-CT ones (≈ 0 eV).

Turning to dipole moments, in Fig. 1(f), we plot the relative dipole moments of the excited states, $|\vec{\mu}_{\text{rel}}| = |\vec{\mu}_{\text{ex}} - \vec{\mu}_{\text{gs}}|$, comparing VOO-CIS-G(12, 2) with CIS. Whereas CIS predicts $|\vec{\mu}_{\text{rel}}|$ values that change continuously from non-CT through weak CT states to strong CT states, again VOO-CIS predicts a completely bimodal distribution of dipole moments: there are CT states with large dipole moments and there are non-CT states with small dipole moments. As such, VOO-CIS yields an extremely intuitive picture of the valence excited states.

In the end, this PYCM data suggests that, by re-diagonalizing the Hamiltonian matrix instead of applying perturbation theory, VOO-CIS is not limited by the failure of CIS for treating CT states.

Twisted ethylene. Twisted ethylene is a paradigmatic example of an avoided crossing.¹⁴ at 90° , the π and π^* orbitals come together in energy. As a result there are three low-lying singlet states, with roughly π^2 , $\pi\pi^*$, and $(\pi^*)^2$ character.¹⁵ To assess the VOO-CIS approach, we plot in Fig. 2, the relative energy of the first few excited states along the torsional angle τ from 60° to 120° , with geometries from Casanova and Head-Gordon.¹⁶

In Fig. 2(a)–2(c), we plot low-lying excitation energies from VOO-CIS-G(n , 2) with $n = 5, 6, 7$, and 14. Note how a new excited state appears in our model Hamiltonian as n goes from 5 to 7; this is the doubly excited $(\pi^*)^2$ state and its appearance suggests that VOO-CIS can predict some doubly excited states (though perhaps only serendipitously). Observe also that increasing the basis beyond $n = 7$ yields no big changes (see $n = 14$). Altogether, this implies that, for an accurate description of the first n' states, the parameter n in VOO-CIS-C(n , m) does not have to be much bigger than n' .

In Fig. 2(d), we plot VOO-CIS-X(14, 3) data versus SF-XCIS¹⁶ data (shown in red). SF-XCIS effectively introduces a π - π^* active space and should be extremely accurate for this problem. The figure suggests that VOO-CIS finds accurate relative energies among the excited states (although VOO-CIS overestimates the ground states by roughly 0.5 eV compared to SF-XCIS). In Fig. 2(e), we plot the CIS/ E_{HF} and CIS(D)/MP2 data, which totally miss the doubly excited state and ignore coupling with the ground-state. (The SOS-CIS(D₀) results closely follow the CIS(D) energies.) From this data, we tentatively conclude that VOO-CIS is stable near avoided crossings, with the added possibility of doubly-excited states.

In Fig. 2(f), we plot the dependence of VOO-CIS-X(n , 3) energies upon the number of states n (for the $\tau = 80^\circ$ geometry). S_0 is the ground state, while S_i ($i = 1, 2$) is the i th

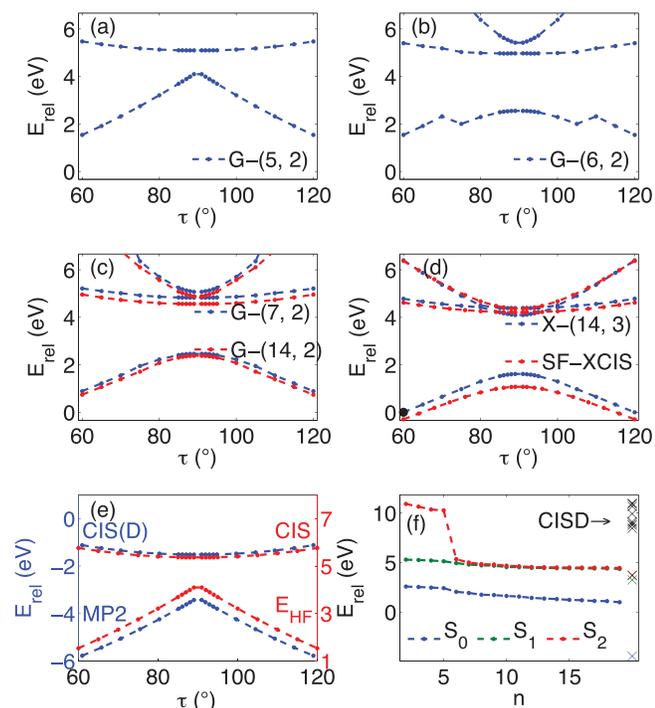


FIG. 2. (a)–(d) Plot of VOO-CIS energies for ethylene along the torsional angle τ , with different VOO-CIS options. (d) The SF-XCIS¹⁶ active-space result (in red). (e) CIS/ E_{HF} and CIS(D)/MP2 data. (f) The VOO-CIS- $X(n, 3)$ energy as a function of n at $\tau = 80^\circ$, compared with CISD data (x's). All energies are relative to the ground state at $\tau = 60^\circ$ in (d) (black solid dot). Note that VOO-CIS is able to find the low-lying doubly excited state.

excited state. On the far right, we plot CISD data (which is equivalent to VOO-CIS- $X(\infty, 3)$). Note that (i) VOO-CIS energies does not depend strongly on n and (ii) VOO-CIS excited state energies are close to CISD energies for $n = 15$, but the ground-state energy is still far away. This is likely a feature of our method, because CISD is known to wildly overestimate vertical excitation energies (by over-stabilizing the ground state¹⁷). For instance, compare the CISD data ($E_1^{\text{ex}} \equiv E_{S_1} - E_{S_0} = 7.7$ eV) with the SF-XCIS data (which includes triples, $E_1^{\text{ex}} = 3.4$ eV) and our VOO-CIS- $X(14,3)$ data ($E_1^{\text{ex}} = 3.2$ eV). Altogether, Fig. 2(f) suggests that we can get reasonable potential energy surface for n not too big or too small.

IV. CONCLUSIONS AND CAVEATS

VOO-CIS- $C(n, m)$ is a variational, almost black-box approach for solving excited state problems without choosing active space orbitals. The only parameters in our approach are the number of CIS states n and the number of doubles added $\sim n^m$. Thus far, there appears to be little dependence on n , provided n is not too small. This is crucial because the cost goes up quickly with n . In our experience, $m = 2, 3$ convincingly outperforms $m = 1$ when treating state crossings. In all cases, VOO-CIS gives a strong energy correction for CT states, far stronger than is found with perturbation theory. Thus far, the

strongest drawback to VOO-CIS is that the method appears to underestimate Rydberg excitation energies, though this may not be crucial for photochemistry¹⁸ especially in the condensed phase.¹⁹

Intensive benchmarking of VOO-CIS is crucial and will be reported shortly. At worst, VOO-CIS is a cheap algorithm to generate approximate CISD energies from an expansion in the doubles space. At best, VOO-CIS is an inexpensive approach for valence CISD energy calculations – where static and dynamic correlation are balanced and vertical excitation energies are not exaggerated. For these reasons, we are currently working on an optimal VOO-CIS algorithm. Because VOO-CIS requires only $O(n^2 N_o N_v)$ memory (e.g., to represent θ_{ai}^{IJ}) and the number of important excited states is often small (e.g., $n \leq 10$), a VOO-CIS algorithm should be highly parallelizable and quite affordable for big molecules. If such an algorithm can be implemented, VOO-CIS methods will have a strong impact on excited state calculations, where new methods are sorely needed.

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