

Low-cost molecular excited states from a state-averaged resonating Hartree–Fock approach

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Abstract

Quantum chemistry methods that describe excited states on the same footing as the ground state are generally scarce. In previous work, Gill et al. (*J. Phys. Chem. A* **112**, 13164 (2008)) and later Sundstrom and Head-Gordon (*J. Chem. Phys.* **140**, 114103 (2014)) considered excited states resulting from a non-orthogonal configuration interaction (NOCI) on stationary solutions of the Hartree–Fock equations. We build upon those contributions and present the state-averaged resonating Hartree–Fock (sa-ResHF) method, which differs from NOCI in that spin-projection and orbital relaxation effects are incorporated from the onset. Our results in a set of small molecules (alanine, formaldehyde, acetaldehyde, acetone, formamide, and ethylene) suggest that sa-ResHF excitation energies are a notable improvement over configuration interaction singles (CIS), at a mean-field computational cost. The orbital relaxation in sa-ResHF, in the presence of a spin-projection operator, generally results in excitation energies that are closer to the experimental values than the corresponding NOCI ones.

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I. INTRODUCTION

The accurate description of electronically excited states has been a long standing quest in quantum chemistry. Time-dependent density functional theory offers a reasonable compromise of computational cost vs accuracy for low-lying excited states. Unfortunately, it is often unreliable as it tends to overstabilize charge-transfer states. Configuration interaction singles (CIS) is often the simplest wavefunction method to treat excited states. But it too is unreliable because it lacks electron correlation as well as orbital relaxation effects. There have been recent efforts to develop alternative, low-cost methods to describe excited states. For instance, Liu *et al.* developed an orbital-optimized CIS strategy where not only the CIS amplitudes but also the orbitals are relaxed [1]. Shea and Neuscamman considered a CIS expansion with an alternative Lagrangian that targets excited states [2].

Some of us had previously explored an excited variation after mean-field projection (VAMP) strategy that provides access, at mean-field computational cost, to the low-energy spectrum of molecular systems. While we were able to describe the low-energy excited states of formaldehyde, we think that the excitation energies afforded may in general be affected because of the use of different ansätze for each of the excited states.

As a motivation for this work, Gill and co-workers [3] noted that higher-lying self-consistent field (SCF) or Hartree–Fock (HF) solutions can provide a reasonably accurate zeroth order description of low-energy excited states. This is even when ignoring the fact that such higher-lying SCF solutions have non-zero overlap with the ground state and cannot be considered, in principle, as true excited state wavefunctions. The authors pointed out, nevertheless, that the overlap remained small in the systems they considered.

In subsequent work, Sundstrom and Head-Gordon [4] expanded on the previous work in their non-orthogonal configuration interaction (NOCI) calculations of the low-energy spectrum of polyene chains. Two important modifications were done with respect to the work of Gill *et al.* First, they performed the actual diagonalization of the Hamiltonian among the set of SCF solutions rather than neglecting the non-zero overlap. Second, they carried out the spin-projection of all the states. The importance of spin-projection cannot be underestimated: low-energy excited states tend to be dominated by single excitations and such excitations out of a reference restricted HF (RHF) determinant necessarily break spin symmetry and are therefore spin-contaminated.

NOCI solutions can often outperform time-dependent HF and CIS because they incorporate orbital relaxation effects, which are completely neglected at the singles excitation level, and because they can formally access doubly-excited determinants: it is possible that one of the low-lying SCF solutions can be mostly characterized as a double-excitation out of the reference HF wavefunction.

Our intention with this work is to explore an ingredient that is still missing: the orbital relaxation of each of the determinants participating in the NOCI solutions in the presence of each other and the spin-projection operator. To this end, we present the result of state-averaged resonating Hartree–Fock (ResHF) solutions. Here, ResHF is our preferred way to call the orbitally optimized multi-determinantal Hartree–Fock solutions which Fukutome introduced in the context of accounting for ground state correlations.

The rest of the paper is organized as follows. In Sec. II we provide details of the formalism we use, including how the variational optimization is carried out. In Sec. III we provide some of the computational details underlying our work. Section IV presents our calculated vertical excitation energies and oscillator strengths for alanine, formaldehyde, acetaldehyde, acetone, and formamide as representative examples of small organic molecules. Lastly, in Sec. V we present our conclusions from this work.

II. FORMALISM

A. Excited VAMP

In Ref. 5, we proposed the use of the excited variation after mean-field projection (VAMP) strategy to obtain the low-energy spectrum of molecular systems. We now proceed to a brief description of it, disregarding the symmetry projection to simplify the presentation. In its simplest form, a single Slater determinant is used for each state. Let us assume that the ground state determinant $|\Phi^0\rangle$ has already been found; we equate $|\Psi^0\rangle \equiv |\Phi^0\rangle$, where the notation implies that the $|\Psi^0\rangle$ state is chosen as the ground state determinant $|\Phi^0\rangle$.

The excited VAMP strategy proposes an ansatz for the first excited state $|\Psi^1\rangle$ as

$$|\Psi^1\rangle = \left(1 - \hat{S}^1\right) |\Phi^1\rangle, \tag{1}$$

where $|\Phi^1\rangle$ is a single Slater determinant and \hat{S}^1 is a projector

$$\hat{S}^1 = \frac{|\Phi^0\rangle\langle\Phi^0|}{\langle\Phi^0|\Phi^0\rangle} \quad (2)$$

that guarantees orthogonality with respect to the ground state. While the ansatz used for the first excited state is not strictly a Slater determinant, all the flexibility in the ansatz is determined by the orbitals that define $|\Phi^1\rangle$. In our previous work, we opted for a variational optimization of the proposed ansatz.

Naturally, the procedure described above for the first excited state can be generalized to higher ones. Let us assume that the ground state and $q - 1$ excited states are already available. An ansatz for the q -th excited state is written as

$$|\Psi^q\rangle = (1 - \hat{S}^q) |\Phi^q\rangle, \quad (3)$$

where $|\Phi^q\rangle$ is a single Slater determinant and \hat{S}^q is the projector

$$\hat{S}^q = \sum_{r,s=0}^{q-1} |\Phi^r\rangle (A^{-1})_{rs} \langle\Phi^s|, \quad (4)$$

$$A_{rs} = \langle\Phi^r|\Phi^s\rangle. \quad (5)$$

In this case, all the variational flexibility of the ansatz lies in the determinant $|\Phi^q\rangle$.

While we successfully used the excited VAMP strategy in Ref. 5, the different ansätze used for different states (due to the form of the projection operator) can lead to an imbalanced description.

B. Non-Orthogonal Configuration Interaction (NOCI)

An alternative strategy to obtain the low energy spectrum of a molecular system based on non-orthogonal determinants is NOCI. For our purposes, NOCI is simply the diagonalization of the Hamiltonian matrix among a set of available, non-orthogonal in general, Slater determinants. That is, given a manifold $\{|\Phi^r\rangle; r = 0, \dots, q\}$ of Slater determinants, NOCI states will result from the solution to the generalized eigenvalue problem

$$\mathbf{H} \mathbf{f} = \mathbf{A} \mathbf{f} \epsilon \quad (6)$$

$$H_{rs} = \langle\Phi^r|\hat{H}|\Phi^s\rangle, \quad (7)$$

$$A_{rs} = \langle\Phi^r|\Phi^s\rangle, \quad (8)$$

where \mathbf{f} is the matrix of eigenvectors and $\boldsymbol{\epsilon}$ is the (diagonal) matrix of eigenvalues. The p -th excited state is then expanded as

$$|\Psi^p\rangle = \sum_{k=0}^q f_{kp} |\Phi^k\rangle. \quad (9)$$

NOCI can provide a reasonable description of the low-energy spectrum of a molecule if each of the determinants approximately describes one of the low-lying states. Here, we emphasize the importance of Gill and co-worker’s contribution [3] realizing that higher-lying SCF solutions can provide an approximate description of an excited state. In retrospect, this is not too surprising given that a CIS state dominated by a single natural transition can often be approximated as a single Slater determinant.

Some of us have used a similar ansatz in a different context, to account for ground state correlations [6]. In that case, the ground state is expanded as

$$|\Psi^0\rangle = \sum_{k=0}^q f_{k0} |\Phi^k\rangle. \quad (10)$$

where the coefficients f_{k0} and determinants $|\Phi^k\rangle$ are variationally optimized to make the ground state energy as low as possible. This ansatz was proposed by Fukutome [7] as the resonating Hartree–Fock (ResHF) method. Note that the nature of the determinants that are optimal to describe ground-state correlations will generally be very different than those determinants that can provide a reasonable description of low-energy excited states.

C. State-Averaged Resonating Hartree–Fock (sa-ResHF)

In this work, we use the same ansatz as that used in NOCI, but we include the optimization of the underlying Slater determinant manifold $\{|\Phi^r\rangle; r = 0, \dots, q\}$. To this purpose, we follow the state-averaged (SA) strategy commonly used in multi-configurational self-consistent field (MC-SCF) approaches and introduce the SA Lagrangian

$$\mathcal{L} = \sum_{j=0}^p w_j \epsilon_j \quad (11)$$

where w_j is the weight of state j in \mathcal{L} (with the condition $w_j > 0$) and ϵ_j is the energy of the j -th state. Note that $p \leq q$, that is only the first p states are included in the Lagrangian, with the rest being discarded.

In order to carry out the minimization of \mathcal{L} with respect to the determinants $\{|\Phi^r\rangle\}$ we follow a similar strategy as that used in Ref. 6, where a Thouless matrix Z^r is used to parametrize each determinant in the expansion. At convergence, the orbital gradient vanishes, i.e.,

$$\frac{\partial}{\partial Z_{ai}^r} \mathcal{L} = \sum_j w_j \frac{\sum_s f_{rj}^* f_{sj} \langle (\Phi^r)_i^a | \hat{H} - \epsilon_j | \Phi^s \rangle}{\sum_{st} f_{tj}^* f_{sj} \langle \Phi^t | \Phi^s \rangle} = 0 \quad \forall \quad r, a, i. \quad (12)$$

Here, $|(\Phi^r)_i^a\rangle$ denotes a single excitation of determinant $|\Phi^r\rangle$.

The equal weight for all states of interest in the sa-ResHF Lagrangian (Eq. 11) helps to avoid selective optimization of one state: there is no risk to fall back to the ResHF expansion of the ground state. In addition, each state is fundamentally described by the same ansatz, which should lead to a more balanced approach than the one used in excited VAMP.

D. Symmetry-Projection

Symmetry-projection can be incorporated in a way that results in only minor modifications of the formalism introduced above. As described in detail in Ref. 8, spin-projection to a state with spin j can be obtained using the operator

$$\hat{P}_{mk}^j = \frac{2j+1}{8\pi^2} \int d\Omega D_{mk}^{s*}(\Omega) \hat{R}(\Omega), \quad (13)$$

where $\Omega = (\alpha, \beta, \gamma)$ stands for the set of Euler angles, D_{mk}^s is an element of Wigner's D-matrix, and $\hat{R}(\Omega)$ is a spin-rotation operator. The evaluation of symmetry projected matrix elements such as overlaps can be carried out as

$$A_{rs} = \sum_{kk'} f_k f_{k'} \langle \Phi^r | \hat{P}_{kk'}^j | \Phi^s \rangle, \quad (14)$$

where f_k are linear coefficients. In this work, we restrict ourselves to the use of UHF determinants (which preserve m_s as a good quantum number). This has two consequences: the double sum over k and k' elements in Eq. 14 collapses to a single term, and the three-dimensional integration from Eq. 13 reduces to a one-dimensional integration, i.e.,

$$A_{rs} = \frac{2j+1}{2} \int_0^\pi d\beta \sin(\beta) d_{mm}^s(\beta) \langle \Phi^r | \exp(-i\beta \hat{S}_y) | \Phi^s \rangle, \quad (15)$$

where we have assumed that determinants $|\Phi^r\rangle$ and $|\Phi^s\rangle$ have both $m_s = m$. The integration can be carried out numerically using a small number of grid points. Note that, since

$\exp(-i\beta\hat{S}_y)|\Phi^s\rangle$ is itself a Slater determinant, Eq. 15 reduces to a weighted sum of overlaps over non-orthogonal determinants. The orbital optimization of the sa-ResHF Lagrangian including spin-projection is not much different from the one shown in Eq. 12: each matrix element is substituted by the projected version in an analogous form to Eq. 15.

III. COMPUTATIONAL DETAILS

The sa-ResHF (including spin projection) calculations have been performed with an in-house code, supplied with one- and two-electron integrals evaluated with the Gaussian 16 suite of programs.[9] In all cases, the (ground state) geometries were optimized with RB3LYP and a cc-pVDZ basis set using Gaussian 16. In the case of alanine, we used the lowest energy conformer as described in the literature.[10] For all our excited state calculations we use the aug-cc-pVDZ basis set. While a larger basis set may be desired to reach better convergence of Rydberg excitations, our current code requires all two-electron integrals to be available in memory. We do not think, however, that the basis set limitation will change the conclusions of this work. We used a 6-point quadrature grid to carry out the spin projection in all cases.

Following Gilbert *et al.*,[3] the initial guess for sa-ResHF calculations consisted of the RHF ground state along with other higher energy SCF solutions. In previous works, such higher energy SCF solutions have been obtained using the maximum overlap method (MOM). In our case, we obtained those solutions in a different way: having carried out a CIS calculation, we prepared initial guesses of excited determinants by using the natural transition orbitals with largest weight for each low-lying CIS solution. We fed such SCF initial guesses (necessarily of UHF type) to a HF solver using a Newton-Raphson (NR) procedure. It is known that NR tends to converge to the closest stationary point, which may or may not be a local minimum. In most instances, we were able to reach stationary SCF solutions with energy higher than that of the starting reference HF without difficulty.

While our current in-house code does not support symmetry, the sa-ResHF optimizations were performed taking advantage of the determinant symmetry in an ad-hoc way. All determinants sharing identical symmetry were optimized simultaneously, but independently from other. Once each symmetry block of determinants were optimized, the entire Hamiltonian was diagonalized to produce the state averaged energies. The overlap between symmetrically-distinct determinants was checked to be zero prior to and after optimization.

IV. RESULTS AND DISCUSSION

We discuss our results for the alanine, formaldehyde, acetaldehyde, acetone, formamide, and ethylene molecules. In what follows, we will use the acronym NOCI to refer to calculations that include spin-projection and the solution to the generalized eigenvalue problem, but use determinants obtained from higher energy SCF solutions. In contrast, the acronym sa-ResHF will be used for calculations that include spin-projection and where the solution to the generalized eigenvalue problem accounts for orbital relaxation effects. Note that NOCI results lack orbital relaxation due to both spin-projection and the presence of other determinants.

A. Alanine

We begin by considering the case of singlet excitations in alanine, which we use for illustrative purposes. We initialize the sa-ResHF calculation with the higher-energy SCF solutions, obtained as described in Sec. III, used in NOCI. We present in Table I the overlap between each of the converged HF solutions after spin-projection. (The raw overlaps are in agreement with those obtained using the MOM method and presented in Ref. 3.)

Table I presents the overlap and Hamiltonian matrices obtained before and after the SA orbital relaxation is carried out. While most overlaps are below ≈ 0.1 (in absolute value) before the optimization, the overlap between determinants 3^1A and 5^1A is around 0.35. The magnitude of this overlap is minimally affected by the presence of the spin projection operator. The presence of such large off-diagonal overlap matrix elements makes imperative the solution to the generalized eigenvalue problem in order to obtain true Hamiltonian eigenvalues in the subspace of interest. We also show in Table I the calculated overlaps after the orbital optimization step has been completed as a proxy for how the orbital optimization modified the original determinants obtained as HF solutions. While this is only a proxy, we do observe that the resulting overlap matrix is different, in this case becoming more diagonally dominant. The excitation energies, obtained as solutions to the sa-ResHF generalized eigenvalue problem, are shown in Table II.

The excitation energies of alanine using the sa-ResHF are in good agreement with previous work. The EOM-CCSD calculations in Ref. 11 agree well with the sa-ResHF energies: the

TABLE I. Overlap and Hamiltonian (in a.u.) matrix elements for alanine using 6 lowest “singlet” ($m_s = 0$) spin-projected HF determinants before and after orbital relaxation.

| State | 1 ¹ A | 2 ¹ A | 3 ¹ A | 4 ¹ A | 5 ¹ A | 6 ¹ A |
|----------------------|------------------|----------------------|------------------|------------------|------------------|------------------|
| NOCI overlap | | | | | | |
| 1 ¹ A | 1.000 | | | | | |
| 2 ¹ A | 0.001 | 1.000 | | | | |
| 3 ¹ A | 0.017 | -0.001 | 1.000 | | | |
| 4 ¹ A | 0.006 | -0.002 | -0.044 | 1.000 | | |
| 5 ¹ A | 0.042 | -0.129 | -0.359 | 0.010 | 1.000 | |
| 6 ¹ A | 0.082 | 0.091 | -0.070 | -0.080 | -0.111 | 1.000 |
| NOCI Hamiltonian | | | | | | |
| 1 ¹ A | -570.961 | | | | | |
| 2 ¹ A | -0.539 | -570.794 | | | | |
| 3 ¹ A | -9.938 | 0.627 | -570.755 | | | |
| 4 ¹ A | -3.336 | 1.379 | 24.952 | -570.725 | | |
| 5 ¹ A | -23.764 | 73.899 | 205.130 | -5.849 | -570.674 | |
| 6 ¹ A | -47.030 | -51.889 | 39.813 | 45.483 | 63.307 | -570.726 |
| sa-ResHF overlap | | | | | | |
| 1 ¹ A | 1.000 | | | | | |
| 2 ¹ A | 0.005 | 1.000 | | | | |
| 3 ¹ A | 0.001 | $-5. \times 10^{-4}$ | 1.000 | | | |
| 4 ¹ A | 0.006 | $2. \times 10^{-5}$ | 0.051 | 1.000 | | |
| 5 ¹ A | 0.066 | -0.001 | 0.027 | 0.014 | 1.000 | |
| 6 ¹ A | 0.031 | 0.034 | -0.012 | 0.004 | 0.011 | 1.000 |
| sa-ResHF Hamiltonian | | | | | | |
| 1 ¹ A | -571.015 | | | | | |
| 2 ¹ A | -3.129 | -570.816 | | | | |
| 3 ¹ A | -0.470 | 0.260 | -570.765 | | | |
| 4 ¹ A | -3.247 | -0.014 | -29.153 | -570.760 | | |
| 5 ¹ A | -37.916 | 0.467 | -15.231 | -8.190 | -570.753 | |
| 6 ¹ A | -17.882 | -19.364 | 7.061 | -2.546 | -6.554 | -570.745 |

major difference is observed for 2¹A where our result is 0.45 eV lower. Other excitation energies deviate from the EOM-CCSD results by approximately 0.1 eV. In contrast, the original calculations by Gill *et al.* (lacking spin-projection and diagonalization) deviate by as much as 1 eV compared to the EOM-CCSD results. We emphasize that the computational cost of the sa-ResHF presented in this work has the same scaling as the one from the original NOCI calculations: there is a global n_{grid} pre-factor (associated with the spin-projection) and a quadratic dependence on the number of determinants used (as opposed to linear), but the mean-field scaling is unchanged.

TABLE II. Vertical singlet excitation energies (in eV) for alanine obtained from solving the spin-projected ResHF eigenvalue problem before and after the SA orbital optimization step.

| state | HF ^a | NOCI | sa-ResHF |
|------------------|--------------------------|------|----------|
| 1 ¹ A | -321.925346 ^b | — | — |
| 2 ¹ A | 4.65 | 4.54 | 5.51 |
| 3 ¹ A | 5.62 | 5.62 | 6.60 |
| 4 ¹ A | 6.47 | 6.38 | 7.40 |
| 5 ¹ A | 6.49 | 6.50 | 7.52 |
| 6 ¹ A | 7.97 | 8.26 | 7.54 |

^a Excitation energies obtained from the various stationary HF solutions (without spin projection).

^b Ground state reference energy (in a.u.).

B. Carbonyls

Tables III through V show the calculated vertical excitation energies resulting from sa-ResHF calculations in formaldehyde, acetaldehyde, and acetone. For these molecules, we considered both singlet and triplet excitations. In general, we observe that the predicted sa-ResHF excitation energies for singlet states are in better agreement with the available experimental values than the corresponding NOCI excitation energies. For both formaldehyde and acetaldehyde we see particularly good agreement with experimental values. In those cases, sa-ResHF excitation energies are in better agreement with experiment than those predicted with CIS, which tends to underestimate the excitation energies.

The sa-ResHF calculations of the triplet states also agree well with experiment, and provide a substantial improvement over NOCI as well as CIS excitation energies. In addition to calculating the triplet states using UHF “triplet” ($m_s = 1$) determinants, we also calculated triplet excitations using UHF “singlet” ($m_s = 0$) determinants, projected to a triplet state in the spin-projection step. The latter excitation energies were consistently higher in energy than those calculated with the triplet determinants, although the magnitude of the difference varied from a few tenths of an eV to over an eV. In general, we expect that NOCI results using “singlet” determinants will be relatively poor: the stable HF solutions are most likely optimized targeting an average of singlet and triplet excitation energies and may

TABLE III. Vertical singlet and triplet excitation energies (in eV) for formaldehyde obtained from NOCI and sa-ResHF calculations. Calculated oscillator strengths are shown in parentheses.

| state | transition | NOCI | sa-ResHF | CIS | exptl ^a |
|---|--------------------|-------|---------------|---------------|----------------------------|
| singlet states | | | | | |
| 1 ¹ A ₁ | | 0.00 | 0.00 | 0.00 | 0.00 |
| 2 ¹ A ₁ | n→3pb ₂ | 6.92 | 7.74 (0.039) | 9.54 (0.117) | 8.14 (0.017 ^b) |
| 3 ¹ A ₁ | π→π* | 10.96 | 10.46 (0.214) | 9.85 (0.173) | |
| 1 ¹ A ₂ | n→π* | 2.71 | 3.60 (0.000) | 4.61 (0.000) | 4.07 |
| 2 ¹ A ₂ | n→3pb ₁ | 7.56 | 8.30 (0.000) | 10.14 (0.000) | 8.37 |
| 1 ¹ B ₁ | σ→π* | 8.22 | 9.27 (0.008) | 10.03 (0.000) | 9.0 ^b |
| 1 ¹ B ₂ | n→3sa ₁ | 5.97 | 6.77 (0.014) | 8.51 (0.032) | 7.11 (0.028 ^b) |
| 2 ¹ B ₂ | n→3pa ₁ | 7.03 | 7.79 (0.026) | 9.39 (0.050) | 7.97 (0.032 ^b) |
| triplet states (using $m_s = 1$ determinants) | | | | | |
| 1 ³ A ₁ | π→π* | 4.44 | 5.74 | 5.07 | 5.86 |
| 2 ³ A ₁ | n→3pb ₂ | 6.94 | 8.15 | 9.20 | 7.96 |
| 1 ³ A ₂ | n→π* | 2.54 | 3.84 | 3.79 | 3.50 |
| 1 ³ B ₁ | σ→π* | 7.36 | 8.62 | 8.70 | |
| 1 ³ B ₂ | n→3sa ₁ | 5.99 | 7.17 | 8.14 | 6.83 |
| 2 ³ B ₂ | n→3pa ₁ | 6.97 | 8.10 | 9.03 | 7.79 |
| triplet states (using $m_s = 0$ determinants) | | | | | |
| 1 ³ A ₁ | π→π* | 5.50 | 5.94 | 5.07 | 5.86 |
| 2 ³ A ₁ | n→3pb ₂ | 7.04 | 8.46 | 9.20 | 7.96 |
| 1 ³ A ₂ | n→π* | 2.59 | 3.97 | 3.79 | 3.50 |
| 2 ³ A ₂ | n→3pb ₁ | 7.81 | 9.15 | 10.05 | |
| 1 ³ B ₁ | σ→π* | 7.59 | 8.98 | 8.70 | |
| 1 ³ B ₂ | n→3sa ₁ | 6.09 | 7.49 | 8.14 | 6.83 |
| 2 ³ B ₂ | n→3pa ₁ | 7.10 | 8.47 | 9.03 | 7.79 |

^a Experimental energies from Ref. [12] unless otherwise noted.

^b Ref. [13]

TABLE IV. Same as Table III, but for acetaldehyde.

| state | NOCI | sa-ResHF | | CIS | | exptl ^a |
|---|-------|----------|--------------------------|-------|--------------------------|--------------------|
| singlet states | | | | | | |
| 1 ¹ A' | 0.00 | 0.00 | | 0.00 | | |
| 2 ¹ A' | 5.84 | 6.81 | (0.026) | 8.43 | (0.017) | 6.82 |
| 3 ¹ A' | 6.55 | 7.53 | (0.063) | 9.19 | (0.110) | 7.46 |
| 4 ¹ A' | 6.92 | 7.90 | (0.013) | 9.40 | (0.031) | 7.75 |
| 5 ¹ A' | 10.88 | 8.71 | (0.007) | 9.90 | (0.330) | |
| 1 ¹ A'' | 3.07 | 4.12 | (8. × 10 ⁻⁶) | 5.01 | (1. × 10 ⁻⁴) | 4.28 |
| 2 ¹ A'' | 6.76 | 7.81 | (0.034) | 9.44 | (0.013) | |
| 3 ¹ A'' | 8.43 | 9.58 | (0.006) | 10.08 | (0.000) | |
| triplet states (using $m_s = 1$ determinants) | | | | | | |
| 1 ³ A' | 4.66 | 6.13 | | 5.36 | | 5.99 |
| 2 ³ A' | 5.80 | 7.15 | | 8.11 | | 6.81 |
| 3 ³ A' | 6.52 | 7.89 | | 8.86 | | 7.44 |
| 4 ³ A' | 6.88 | 8.23 | | 9.24 | | 7.8 |
| 1 ³ A'' | 2.93 | 4.39 | | 4.24 | | 3.97 |
| 2 ³ A'' | 6.83 | 8.18 | | 8.88 | | |
| 3 ³ A'' | 7.61 | 9.05 | | 9.36 | | |
| triplet states (using $m_s = 0$ determinants) | | | | | | |
| 1 ³ A' | 6.92 | 6.34 | | 5.36 | | 5.99 |
| 2 ³ A' | 7.84 | 7.44 | | 8.11 | | 6.81 |
| 3 ³ A' | 5.76 | 8.20 | | 8.86 | | 7.44 |
| 4 ³ A' | 6.65 | 8.57 | | 9.24 | | 7.8 |
| 1 ³ A'' | 2.99 | 4.58 | | 4.24 | | 3.97 |
| 2 ³ A'' | 5.93 | 8.50 | | 8.88 | | |
| 3 ³ A'' | 7.03 | 9.41 | | 9.36 | | |

^a Experimental energies from Ref. [12]

TABLE V. Same as Table III, but for acetone.

| State | NOCI | sa-ResHF | | CIS | | exptl ^a |
|---|------|----------|---------|------|---------|--------------------|
| singlet states | | | | | | |
| 1 ¹ A ₁ | 0.00 | 0.00 | | 0.00 | | |
| 2 ¹ A ₁ | 6.50 | 5.93 | (0.002) | 9.24 | (0.029) | 7.41 |
| 1 ¹ A ₂ | 3.16 | 2.56 | (0.000) | 5.25 | (0.000) | 4.38 |
| 2 ¹ A ₂ | 6.34 | 5.87 | (0.000) | 9.20 | (0.000) | 7.36 |
| 1 ¹ B ₂ | 5.48 | 4.95 | (0.043) | 8.25 | (0.040) | 6.35 |
| 2 ¹ B ₂ | 6.52 | 5.98 | (0.013) | 9.32 | (0.003) | 7.45 |
| 3 ¹ B ₂ | 7.05 | 6.56 | (0.057) | 9.88 | (0.061) | 8.09 |
| triplet states (using $m_s = 1$ determinants) | | | | | | |
| 1 ³ A ₁ | 4.67 | 4.56 | | 5.52 | | 5.88 |
| 2 ³ A ₁ | 6.33 | 6.18 | | 9.11 | | |
| 1 ³ A ₂ | 3.04 | 2.94 | | 4.51 | | 4.16 |
| 1 ³ B ₂ | 5.48 | 5.28 | | 8.09 | | |
| 2 ³ B ₂ | 6.52 | 6.30 | | 9.20 | | |
| 3 ³ B ₂ | 7.07 | 6.93 | | 9.74 | | |
| triplet states (using $m_s = 0$ determinants) | | | | | | |
| 2 ³ A ₁ ^b | 6.51 | 6.48 | | 9.11 | | |
| 1 ³ A ₂ | 3.11 | 3.13 | | 4.51 | | 4.16 |
| 2 ³ A ₂ | 6.47 | 6.49 | | 9.11 | | |
| 1 ³ B ₂ | 5.59 | 5.57 | | 8.09 | | |
| 2 ³ B ₂ | 6.64 | 6.62 | | 9.20 | | |
| 3 ³ B ₂ | 7.18 | 7.21 | | 9.74 | | |

^a Experimental energies from Ref. [14]

^b Even though we do not have a 1 ³A₁ state, we have labeled this as 2 ³A₁ given the character of the transition.

in general be better for the singlet states. However, sa-ResHF calculations further relax the orbitals in the presence of both the spin-projection operator and the full manifold of determinants. We speculate that for some states with large multi-reference character the “singlet” determinants may work better, but otherwise the “triplet” determinants may prove superior.

The sa-ResHF excitation energies are generally superior to the corresponding NOCI results, suggesting that the orbital optimization provides a significant improvement. As an example, the NOCI and sa-ResHF excitation energies for the 1A_1 states in formaldehyde are significantly different. This highlights the importance of the orbital relaxation effect.

The oscillator strengths for formaldehyde from sa-ResHF and CIS calculations as well as the experimental ones (when available) are shown in Table III. The oscillator strength values are mildly correlated between the three sources. While there are large discrepancies between sa-ResHF and CIS, both methods qualitatively match the experimental values, with the $2\,{}^1A_1$, $1\,{}^1B_2$, and $2\,{}^1B_2$ having small oscillator strengths.

While Both CIS and sa-ResHF predict a very bright $3\,{}^1A_1$ state, it is known that the $\pi \rightarrow \pi^*$ transition in formaldehyde can have significant mixing with Rydberg excitations. [13]. The basis set employed in this study is not well suited to handle states with significant Rydberg mixing, although we still find good agreement between the sa-ResHF calculated excitation energy of 10.43 eV and the 10.1 eV value predicted using a time-dependent HF approach.[13]

The sa-ResHF excitation energies for acetaldehyde have good agreement with experimental values for the singlet states with the largest error being around 0.15 eV (see Table IV). Other excitation energies show larger deviations from the experimental values. Similar trends are observed for the triplet states, with the sa-ResHF excitation energies being slightly worse than for the singlet states. There is qualitative agreement between CIS and sa-ResHF oscillator strengths, with the notable exception of the $5\,{}^1A'$ state: CIS predicts it to be bright as opposed to sa-ResHF. This is simply a reflection of the different character between the CIS and sa-ResHF states.

The sa-ResHF excitation energies for acetone show the largest deviation from experimental values for all carbonyl systems tested, with all excitations having an average negative deviation of approximately 1.5 eV (see Table V). The sa-ResHF excitation energy errors are consistent between all experimental excited states. This can be due to a significant dif-

ference in the dynamical correlation contributions to the ground state and all the low-lying excited states and/or to the fact that low-lying excited states have significant multi-reference character.

C. Formamide

We show in Table VI the calculated vertical excitation energies in formamide. Formamide has two main singlet valence transitions, the $n \rightarrow \pi^*$ and the $\pi \rightarrow \pi^*$. The sa-ResHF excitation energy for the $n \rightarrow \pi^*$ transition (5.54 eV) agrees well with experimental value reported in the literature (5.65 eV) (see Table VI). This can be compared to the fairly poor CIS excitation energy of 6.55 eV. This state has also been well described by previous CASPT2 calculations and coupled cluster calculations coming within a few tenths of an eV.[15]

The $\pi \rightarrow \pi^*$ singlet state has proven more challenging to accurately describe theoretically.[16, 17] The state is known to have significant amount of mixing with the Rydberg states $n \rightarrow s$ and $n \rightarrow 3p_\pi$. [16–18] The sa-ResHF excitation energy is 7.95 eV, which is in good agreement with the experimental value of 7.32 eV.[16] This error compares favorably to other theoretical methods used to study these transitions. Schreiber *et al.* employed CASPT2 (7.44 eV) and various coupled cluster methods (8.27 eV using CC3) and found significant deviations in the calculation of the $\pi \rightarrow \pi^*$ state and very accurate energies with both CASPT2 and the CC methods for the $n \rightarrow \pi^*$. [15] This state was also studied by Gilbert *et al.* using the maximum overlap method (MOM) with the B3LYP functional giving energies for the $n \rightarrow \pi^*$ and the $\pi \rightarrow \pi^*$ states of 5.22 eV and 6.29 eV respectively.

Oscillator strengths were also found to be in qualitative agreement with other methods and experiment. The sa-ResHF value for the $\pi \rightarrow \pi^*$ state matches that of the experimental value within the precision of the experimental measurements (0.37).[16] Previous CASPT2, CC, and CASSCF/MRCI calculations also provide a similar oscillator strength as well as confirming the near zero oscillator strength of the $n \rightarrow \pi^*$ transition.[15, 17, 18]. The experimental methods confirm the experimental observation of the two valence transitions having a dark state and a bright state.

TABLE VI. Same as Table III, but for formamide.

| state | NOCI | sa-ResHF | | CIS | | exptl ^a | |
|---|------|----------|---------|------|------------------------|--------------------|--------|
| singlet states | | | | | | | |
| 1 ¹ A' | 0.00 | 0.00 | (0.000) | 0.00 | | | |
| 2 ¹ A' | 7.57 | 6.91 | (0.002) | 8.55 | (0.087) | | |
| 3 ¹ A' | 5.08 | 7.50 | (0.074) | 8.92 | (0.189) | | |
| 4 ¹ A' | 6.50 | 7.95 | (0.368) | 9.43 | (0.140) | 7.32 | (0.37) |
| 1 ¹ A'' | 5.70 | 5.54 | (0.001) | 6.55 | (0.001) | 5.65 | |
| 2 ¹ A'' | 6.22 | 6.26 | (0.022) | 7.67 | (0.023) | | |
| 3 ¹ A'' | 4.27 | 7.13 | (0.001) | 8.59 | (1.×10 ⁻⁴) | | |
| 4 ¹ A'' | 5.94 | 7.72 | (0.001) | 9.20 | (0.010) | | |
| triplet states (using $m_s = 1$ determinants) | | | | | | | |
| 1 ³ A' | 4.76 | 6.37 | | 5.73 | | | |
| 2 ³ A' | 5.06 | 7.21 | | 8.46 | | | |
| 3 ³ A' | 6.06 | 7.79 | | 9.05 | | | |
| 1 ³ A'' | 5.60 | 5.81 | | 5.90 | | | |
| 2 ³ A'' | 6.21 | 6.53 | | 7.31 | | | |
| 3 ³ A'' | 4.17 | 7.52 | | 8.45 | | | |
| triplet states (using $m_s = 1$ determinants) | | | | | | | |
| 1 ³ A' | 6.49 | 6.63 | | 5.73 | | | |
| 2 ³ A' | 5.77 | 7.40 | | 8.46 | | | |
| 3 ³ A' | 6.31 | 7.99 | | 9.05 | | | |
| 1 ³ A'' | 4.23 | 5.99 | | 5.90 | | | |
| 2 ³ A'' | 5.54 | 7.23 | | 7.31 | | | |
| 3 ³ A'' | 7.07 | 8.19 | | 8.45 | | | |
| 4 ³ A'' | 6.25 | 8.79 | | 9.07 | | | |

^a Experimental energies from Ref.[16]

D. Ethylene

Table VII shows the calculated vertical excitation energies in ethylene. In this case, the sa-ResHF method underestimates energies for both singlet and triplet states. The fact that all excitation energies are underestimated probably reflects an imbalanced description between the ground and the excited states, with the ground state being more poorly described. The degree of error varies between 0.04 eV and 1.12 eV, the largest variance of any system tested. While the sources of error in sa-ResHF calculations in ethylene are the same as in other molecules, we observe that the high symmetry of the molecule plays a role in the quality of the results. Examining the symmetries of each state in VII, nearly all states calculated belong to independent symmetry groups, with the exception of the pairs of the ${}^1B_{1g}$, ${}^3B_{1g}$, and 1A_g states. Since all determinants retained their symmetry during SCF optimization, nearly two-thirds of the excited states calculations contained only a single determinant. This made many excited state calculations equivalent to single-determinant symmetry-projected HF calculations: states of different symmetry do not interact. If the multi-reference character or the dynamical correlation is significantly different between the ground state and states with other symmetry, there is no chance for partial cancellation of errors due to the state-averaged approach.

V. CONCLUSIONS

Building upon the NOCI strategy used by Sundstrom and Head-Gordon, we have presented the sa-ResHF approach for the calculation of excited states in molecular systems. In sa-ResHF, we introduce orbital optimization of a state-averaged Lagrangian in the presence of *both* spin-projection and the Slater determinant manifold.

Our results confirm that in a number of cases the orbital optimization makes a large difference in the predicted excitation energies. Generally, the resulting sa-ResHF excitation energies are in better agreement with experiment than in NOCI, though there are some exceptions.

For the sa-ResHF strategy the major remaining source of error can be attributed to the lack of dynamic correlation. In that regard, these results should be viewed as an alternative to SA complete active space SCF (CAS-SCF) calculations. Both lack dynamic correlation in

TABLE VII. Same as Table III, but for ethylene.

| state | NOCI | sa-ResHF | | CIS | | Exp ^a |
|---|------|----------|---------|------|---------|------------------|
| singlet states | | | | | | |
| 1^1A_g | 0.00 | 0.00 | | 0.00 | | |
| 2^1A_g | 8.46 | 7.85 | (0.000) | 8.85 | (0.000) | 8.26 |
| 1^1A_u | 6.72 | 7.76 | (0.000) | 9.06 | (0.000) | |
| 1^1B_{1g} | 6.04 | 6.68 | (0.000) | 7.81 | (0.000) | 7.80 |
| 2^1B_{1g} | 7.74 | 8.10 | (0.000) | 9.24 | (0.000) | |
| 1^1B_{2g} | 8.53 | 6.73 | (0.000) | 7.99 | (0.000) | |
| 1^1B_{1u} | 6.66 | 7.61 | (0.443) | 7.82 | (0.515) | 7.65 |
| 1^1B_{3u} | 8.09 | 6.05 | (0.116) | 7.21 | (0.092) | 7.11 |
| triplet states (using $m_s = 1$ determinants) | | | | | | |
| 1^3A_g | 3.38 | 7.36 | | 8.17 | | 8.15 |
| 1^3A_u | 5.92 | 7.82 | | 9.04 | | |
| 1^3B_{1g} | 6.62 | 6.71 | | 7.72 | | |
| 2^3B_{1g} | 8.28 | 8.28 | | 8.50 | | |
| 1^3B_{2g} | 7.28 | 6.74 | | 7.86 | | |
| 1^3B_{1u} | 6.66 | 3.38 | | 3.73 | | 4.30 |
| 1^3B_{3u} | 7.74 | 6.00 | | 6.99 | | 6.98 |
| triplet states (using $m_s = 0$ determinants) | | | | | | |
| 1^3A_g | 5.97 | 7.43 | | 8.17 | | 8.15 |
| 1^3A_u | 6.66 | 7.89 | | 9.04 | | |
| 1^3B_{1g} | 4.32 | 6.78 | | 7.72 | | |
| 2^3B_{1g} | 6.70 | 8.37 | | 8.50 | | |
| 1^3B_{2g} | 7.77 | 6.82 | | 7.86 | | |
| 1^3B_{1u} | 7.39 | 3.80 | | 3.73 | | 4.30 |
| 1^3B_{3u} | 8.26 | 6.08 | | 6.99 | | 6.98 |

^a Experimental energies from Ref. [19]

their standard forms, but can provide good reference wavefunctions for post-SCF treatments. We plan to develop approaches that account for the missing dynamic correlation in the near future.

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**Supplemental Materials: Low-cost molecular excited states
from a state-averaged resonating Hartree–Fock approach**

TABLE S1. Energies of HF determinants used in NOCI calculations (without spin projection).

| state | singlet (eV) | state | triplet (eV) |
|--------------|--------------|-------------|--------------|
| formaldehyde | | | |
| 1^1A_1 | -113.884842 | | |
| 2^1A_1 | 6.99 | 1^3A_1 | 4.47 |
| 3^1A_1 | 8.27 | 2^3A_1 | 6.98 |
| 1^1A_2 | 2.70 | 1^3A_2 | 2.58 |
| 2^1A_2 | 7.72 | 1^3B_1 | 7.42 |
| 1^1B_1 | 7.91 | 1^3B_2 | 6.02 |
| 1^1B_2 | 6.04 | 2^3B_2 | 7.01 |
| 2^1B_2 | 7.07 | | |
| formamide | | | |
| $1^1A'$ | -168.963902 | | |
| $2^1A'$ | 5.81 | $1^3A'$ | 4.91 |
| $3^1A'$ | 6.31 | $2^3A'$ | 5.67 |
| $4^1A'$ | 6.95 | $3^3A'$ | 6.28 |
| $1^1A''$ | 4.34 | $1^3A''$ | 4.27 |
| $2^1A''$ | 5.58 | $2^3A''$ | 5.48 |
| $3^1A''$ | 6.50 | $3^3A''$ | 6.48 |
| $4^1A''$ | 7.07 | | |
| ethylene | | | |
| 1^1A_g | -78.043703 | | |
| 2^1A_g | 7.73 | 1^3A_g | 7.29 |
| 1^1A_u | 7.76 | 1^3A_u | 7.75 |
| 1^1B_{1g} | 6.66 | 1^3B_{1g} | 6.64 |
| 2^1B_{1g} | 8.52 | 2^3B_{1g} | 8.39 |
| 1^1B_{2g} | 6.71 | 1^3B_{2g} | 6.67 |
| 1^1B_{1u} | 6.38 | 1^3B_{1u} | 3.47 |
| 1^1B_{3u} | 6.00 | 1^3B_{3u} | 5.94 |
| acetaldehyde | | | |
| $1^1A'$ | -152.938947 | | |
| $2^1A'$ | 5.89 | $1^3A'$ | 4.70 |
| $3^1A'$ | 6.59 | $2^3A'$ | 5.83 |
| $4^1A'$ | 6.98 | $3^3A'$ | 6.55 |
| $5^1A'$ | 8.34 | $4^3A'$ | 6.91 |
| $1^1A''$ | 3.08 | $1^3A''$ | 2.98 |
| $2^1A''$ | 6.83 | $2^3A''$ | 6.84 |
| $3^1A''$ | 8.15 | $3^3A''$ | 7.69 |
| acetone | | | |
| 1^1A_1 | -191.988887 | | |
| 2^1A_1 | 6.54 | 1^3A_1 | 4.80 |
| 1^1A_2 | 3.25 | 2^3A_1 | 6.43 |
| 2^1A_2 | 6.46 | 1^3A_2 | 3.16 |
| 1^1B_2 | 5.60 | 1^3B_2 | 5.58 |
| 2^1B_2 | 6.64 | 2^3B_2 | 6.62 |
| 3^1B_2 | 7.18 | 3^3B_2 | 7.17 |

TABLE S2. Overlap and Hamiltonian Matrix Elements for Formaldehyde (Before Optimization).

| Determinant | 1^1A_1 | 2^1A_1 | 3^1A_1 | 1^1A_2 | 2^1A_2 | 1^1B_1 | 1^1B_2 | 2^1B_2 |
|-------------|------------------------|-----------------------|-----------------------|------------------------|------------------------|-----------------------|------------------------|-----------------------|
| Overlap | | | | | | | | |
| 1^1A_1 | 1.00×10^0 | | | | | | | |
| 2^1A_1 | -2.01×10^{-2} | 4.95×10^{-1} | | | | | | |
| 3^1A_1 | -1.48×10^{-1} | 7.03×10^{-3} | 5.37×10^{-1} | | | | | |
| 1^1A_2 | — | — | — | 4.95×10^{-1} | | | | |
| 2^1A_2 | — | — | — | -4.26×10^{-2} | 4.89×10^{-1} | | | |
| 1^1B_1 | — | — | — | — | — | 4.97×10^{-1} | | |
| 1^1B_2 | — | — | — | — | — | — | 4.94×10^{-1} | |
| 2^1B_2 | — | — | — | — | — | — | -2.65×10^{-2} | 4.93×10^{-1} |
| Hamiltonian | | | | | | | | |
| 1^1A_1 | -1.45×10^2 | | | | | | | |
| 2^1A_1 | 2.91×10^0 | -7.18×10^1 | | | | | | |
| 3^1A_1 | 2.14×10^1 | -1.02×10^0 | -7.79×10^1 | | | | | |
| 1^1A_2 | — | — | — | -7.18×10^1 | | | | |
| 2^1A_2 | — | — | — | 6.19×10^0 | -7.09×10^1 | | | |
| 1^1B_1 | — | — | — | — | — | -7.20×10^1 | | |
| 1^1B_2 | — | — | — | — | — | — | -7.17×10^1 | |
| 2^1B_2 | — | — | — | — | — | — | 3.84×10^0 | -7.15×10^1 |
| | | | | | | | | |
| Determinant | 1^3A_1 | 2^3A_1 | 1^3A_2 | 1^3B_1 | 1^3B_2 | 2^3B_2 | | |
| Overlap | | | | | | | | |
| 1^3A_1 | 3.32×10^{-1} | | | | | | | |
| 2^3A_1 | -8.76×10^{-5} | 3.31×10^{-1} | | | | | | |
| 1^3A_2 | — | — | 3.32×10^{-1} | | | | | |
| 1^3B_1 | — | — | — | 3.31×10^{-1} | | | | |
| 1^3B_2 | — | — | — | — | 3.31×10^{-1} | | | |
| 2^3B_2 | — | — | — | — | -2.22×10^{-2} | 3.30×10^{-1} | | |
| Hamiltonian | | | | | | | | |
| 1^3A_1 | -4.82×10^1 | | | | | | | |
| 2^3A_1 | 1.26×10^{-2} | -4.80×10^1 | | | | | | |
| 1^3A_2 | — | — | -4.82×10^1 | | | | | |
| 1^3B_1 | — | — | — | -4.81×10^1 | | | | |
| 1^3B_2 | — | — | — | — | -4.80×10^1 | | | |
| 2^3B_2 | — | — | — | — | 3.22×10^0 | -4.79×10^1 | | |

TABLE S3. Overlap and Hamiltonian Matrix Elements for Formamide (Before Optimization).

| Determinant | $1^1A'$ | $2^1A'$ | $3^1A'$ | $4^1A'$ | $1^1A''$ | $2^1A''$ | $3^1A''$ | $4^1A''$ |
|-------------|------------------------|------------------------|------------------------|------------------------|------------------------|-----------------------|-----------------------|-----------------------|
| Overlap | | | | | | | | |
| $1^1A'$ | 1.00×10^0 | | | | | | | |
| $2^1A'$ | -3.42×10^{-3} | 4.89×10^{-1} | | | | | | |
| $3^1A'$ | -1.14×10^{-1} | -1.52×10^{-2} | 5.09×10^{-1} | | | | | |
| $4^1A'$ | -3.95×10^{-2} | -5.34×10^{-3} | -5.55×10^{-2} | 4.99×10^{-1} | | | | |
| $1^1A''$ | – | – | – | – | 4.89×10^{-1} | | | |
| $2^1A''$ | – | – | – | – | 0.00×10^0 | 4.61×10^{-1} | | |
| $3^1A''$ | – | – | – | – | 0.00×10^0 | 1.43×10^{-2} | 4.61×10^{-1} | |
| $4^1A''$ | – | – | – | – | 0.00×10^0 | 3.29×10^{-2} | 1.70×10^{-2} | 4.60×10^{-1} |
| Hamiltonian | | | | | | | | |
| $1^1A'$ | -2.40×10^2 | | | | | | | |
| $2^1A'$ | 8.21×10^{-1} | -1.17×10^2 | | | | | | |
| $3^1A'$ | 2.75×10^1 | 3.64×10^0 | -1.22×10^2 | | | | | |
| $4^1A'$ | 9.50×10^0 | 1.28×10^0 | 1.33×10^1 | -1.20×10^2 | | | | |
| $1^1A''$ | – | – | – | – | -1.19×10^2 | | | |
| $2^1A''$ | – | – | – | – | -7.10×10^{-5} | -1.11×10^2 | | |
| $3^1A''$ | – | – | – | – | 1.30×10^{-5} | -3.44×10^0 | -1.11×10^2 | |
| $4^1A''$ | – | – | – | – | 1.67×10^{-4} | -7.89×10^0 | -4.08×10^0 | -1.10×10^2 |
| | | | | | | | | |
| Determinant | $1^3A'$ | $2^3A'$ | $3^3A'$ | $1^3A''$ | $2^3A''$ | $3^3A''$ | | |
| Overlap | | | | | | | | |
| $1^3A'$ | 3.31×10^{-1} | | | | | | | |
| $2^3A'$ | -5.04×10^{-5} | 3.32×10^{-1} | | | | | | |
| $3^3A'$ | -1.37×10^{-5} | 1.45×10^{-2} | 3.32×10^{-1} | | | | | |
| $1^3A''$ | – | – | – | 3.32×10^{-1} | | | | |
| $2^3A''$ | – | – | – | 0.00×10^0 | 3.14×10^{-1} | | | |
| $3^3A''$ | – | – | – | 0.00×10^0 | 1.09×10^{-2} | 3.14×10^{-1} | | |
| Hamiltonian | | | | | | | | |
| $1^3A'$ | -7.94×10^1 | | | | | | | |
| $2^3A'$ | 1.17×10^{-2} | -7.98×10^1 | | | | | | |
| $3^3A'$ | 3.46×10^{-3} | -3.49×10^0 | -7.97×10^1 | | | | | |
| $1^3A''$ | – | – | – | -7.97×10^1 | | | | |
| $2^3A''$ | – | – | – | 3.09×10^{-4} | -7.54×10^1 | | | |
| $3^3A''$ | – | – | – | -2.92×10^{-5} | -2.62×10^0 | -7.53×10^1 | | |

TABLE S4. Overlap and Hamiltonian Matrix Elements for Ethylene (Before Optimization).

| Determinant | 1^1A_g | 2^1A_g | 1^1A_u | 1^1B_{1g} | 2^1B_{1g} | 1^1B_{2g} | 1^1B_{1u} | 1^1B_{3u} |
|-------------|-----------------------|-----------------------|------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Overlap | | | | | | | | |
| 1^1A_g | 1.00×10^0 | | | | | | | |
| 2^1A_g | 7.61×10^{-2} | 5.12×10^{-1} | | | | | | |
| 1^1A_u | — | — | 4.99×10^{-1} | | | | | |
| 1^1B_{1g} | — | — | — | 4.99×10^{-1} | | | | |
| 2^1B_{1g} | — | — | — | 0.00×10^0 | 4.92×10^{-1} | | | |
| 1^1B_{2g} | — | — | — | — | — | 4.99×10^{-1} | | |
| 1^1B_{1u} | — | — | — | — | — | — | 5.00×10^{-1} | |
| 1^1B_{3u} | — | — | — | — | — | — | — | 4.99×10^{-1} |
| Hamiltonian | | | | | | | | |
| 1^1A_g | -1.12×10^2 | | | | | | | |
| 2^1A_g | 8.48×10^0 | -5.69×10^1 | | | | | | |
| 1^1A_u | — | — | -5.55×10^1 | | | | | |
| 1^1B_{1g} | — | — | — | -5.56×10^1 | | | | |
| 2^1B_{1g} | — | — | — | 9.34×10^{-4} | -5.47×10^1 | | | |
| 1^1B_{2g} | — | — | — | — | — | -5.56×10^1 | | |
| 1^1B_{1u} | — | — | — | — | — | — | -5.56×10^1 | |
| 1^1B_{3u} | — | — | — | — | — | — | — | -5.56×10^1 |
| | | | | | | | | |
| Determinant | 1^3A_g | 1^3A_u | 1^3B_{1g} | 2^3B_{1g} | 1^3B_{2g} | 1^3B_{1u} | 1^3B_{3u} | |
| Overlap | | | | | | | | |
| 1^3A_g | 3.33×10^{-1} | | | | | | | |
| 1^3A_u | — | 3.33×10^{-1} | | | | | | |
| 1^3B_{1g} | — | — | 3.33×10^{-1} | | | | | |
| 2^3B_{1g} | — | — | 0.00×10^0 | 3.31×10^{-1} | | | | |
| 1^3B_{2g} | — | — | — | — | 3.33×10^{-1} | | | |
| 1^3B_{1u} | — | — | — | — | — | 3.32×10^{-1} | | |
| 1^3B_{3u} | — | — | — | — | — | — | 3.33×10^{-1} | |
| Hamiltonian | | | | | | | | |
| 1^3A_g | -3.70×10^1 | | | | | | | |
| 1^3A_u | — | -3.70×10^1 | | | | | | |
| 1^3B_{1g} | — | — | -3.71×10^1 | | | | | |
| 2^3B_{1g} | — | — | -3.66×10^{-4} | -3.68×10^1 | | | | |
| 1^3B_{2g} | — | — | — | — | -3.71×10^1 | | | |
| 1^3B_{1u} | — | — | — | — | — | -3.70×10^1 | | |
| 1^3B_{3u} | — | — | — | — | — | — | -3.71×10^1 | |

TABLE S5. Overlap and Hamiltonian Matrix Elements for Acetaldehyde (Before Optimization).

| Determinant | $1^1A'$ | $2^1A'$ | $3^1A'$ | $4^1A'$ | $5^1A'$ | $1^1A''$ | $2^1A''$ | $3^1A''$ |
|-------------|------------------------|------------------------|------------------------|------------------------|-----------------------|------------------------|------------------------|-----------------------|
| Overlap | | | | | | | | |
| $1^1A'$ | 1.00×10^0 | | | | | | | |
| $2^1A'$ | -6.53×10^{-2} | 5.00×10^{-1} | | | | | | |
| $3^1A'$ | -3.66×10^{-2} | -5.55×10^{-2} | 4.97×10^{-1} | | | | | |
| $4^1A'$ | -4.00×10^{-2} | 7.60×10^{-3} | -1.66×10^{-4} | 4.97×10^{-1} | | | | |
| $5^1A'$ | 1.58×10^{-1} | -2.13×10^{-2} | -1.16×10^{-2} | -1.30×10^{-2} | 5.41×10^{-1} | | | |
| $1^1A''$ | – | – | – | – | – | 4.94×10^{-1} | | |
| $2^1A''$ | – | – | – | – | – | 3.57×10^{-2} | 4.95×10^{-1} | |
| $3^1A''$ | – | – | – | – | – | 8.36×10^{-5} | 4.31×10^{-4} | 4.96×10^{-1} |
| Hamiltonian | | | | | | | | |
| $1^1A'$ | -2.23×10^2 | | | | | | | |
| $2^1A'$ | 1.45×10^1 | -1.11×10^2 | | | | | | |
| $3^1A'$ | 8.15×10^0 | 1.23×10^1 | -1.11×10^2 | | | | | |
| $4^1A'$ | 8.91×10^0 | -1.69×10^0 | 3.68×10^{-2} | -1.11×10^2 | | | | |
| $5^1A'$ | -3.52×10^1 | 4.74×10^0 | 2.58×10^0 | 2.89×10^0 | -1.20×10^2 | | | |
| $1^1A''$ | – | – | – | – | – | -1.10×10^2 | | |
| $2^1A''$ | – | – | – | – | – | -7.94×10^0 | -1.10×10^2 | |
| $3^1A''$ | – | – | – | – | – | -1.87×10^{-2} | -9.56×10^{-2} | -1.10×10^2 |
| Determinant | | | | | | | | |
| Determinant | $1^3A'$ | $2^3A'$ | $3^3A'$ | $4^3A'$ | $1^3A''$ | $2^3A''$ | $3^3A''$ | |
| Overlap | | | | | | | | |
| $1^3A'$ | 3.32×10^{-1} | | | | | | | |
| $2^3A'$ | 7.54×10^{-5} | 3.31×10^{-1} | | | | | | |
| $3^3A'$ | 5.79×10^{-6} | -4.06×10^{-2} | 3.31×10^{-1} | | | | | |
| $4^3A'$ | 6.75×10^{-5} | 1.63×10^{-2} | -5.23×10^{-3} | 3.31×10^{-1} | | | | |
| $1^3A''$ | – | – | – | – | 3.32×10^{-1} | | | |
| $2^3A''$ | – | – | – | – | 1.56×10^{-4} | 3.31×10^{-1} | | |
| $3^3A''$ | – | – | – | – | 2.74×10^{-2} | 3.28×10^{-4} | 3.31×10^{-1} | |
| Hamiltonian | | | | | | | | |
| $1^3A'$ | -7.38×10^1 | | | | | | | |
| $2^3A'$ | -1.65×10^{-2} | -7.38×10^1 | | | | | | |
| $3^3A'$ | -1.17×10^{-3} | 9.03×10^0 | -7.37×10^1 | | | | | |
| $4^3A'$ | -1.48×10^{-2} | -3.63×10^0 | 1.16×10^0 | -7.36×10^1 | | | | |
| $1^3A''$ | – | – | – | – | -7.39×10^1 | | | |
| $2^3A''$ | – | – | – | – | 3.47×10^{-2} | -7.37×10^1 | | |
| $3^3A''$ | – | – | – | – | -6.09×10^0 | -7.32×10^{-2} | -7.38×10^1 | |

TABLE S6. Overlap and Hamiltonian Matrix Elements for Acetone (Before Optimization).

| Determinant | 1^1A_1 | 2^1A_1 | 1^1A_2 | 2^1A_2 | 1^1B_2 | 2^1B_2 | 3^1B_2 |
|-------------|------------------------|-----------------------|------------------------|------------------------|------------------------|-----------------------|-----------------------|
| Overlap | | | | | | | |
| 1^1A_1 | 1.00×10^0 | | | | | | |
| 2^1A_1 | 9.25×10^{-2} | 5.04×10^{-1} | | | | | |
| 1^1A_2 | — | — | 4.94×10^{-1} | | | | |
| 2^1A_2 | — | — | -2.83×10^{-2} | 4.97×10^{-1} | | | |
| 1^1B_2 | — | — | — | — | 4.96×10^{-1} | | |
| 2^1B_2 | — | — | — | — | -2.66×10^{-2} | 4.96×10^{-1} | |
| 3^1B_2 | — | — | — | — | 6.06×10^{-3} | 6.94×10^{-3} | 4.96×10^{-1} |
| Hamiltonian | | | | | | | |
| 1^1A_1 | -3.12×10^2 | | | | | | |
| 2^1A_1 | -2.88×10^1 | -1.57×10^2 | | | | | |
| 1^1A_2 | — | — | -1.54×10^2 | | | | |
| 2^1A_2 | — | — | 8.80×10^0 | -1.55×10^2 | | | |
| 1^1B_2 | — | — | — | — | -1.54×10^2 | | |
| 2^1B_2 | — | — | — | — | 8.28×10^0 | -1.54×10^2 | |
| 3^1B_2 | — | — | — | — | -1.89×10^0 | -2.16×10^0 | -1.54×10^2 |
| | | | | | | | |
| Determinant | 1^3A_1 | 2^3A_1 | 1^3A_2 | 1^3B_2 | 2^3B_2 | 3^3B_2 | |
| Overlap | | | | | | | |
| 1^3A_1 | 3.32×10^{-1} | | | | | | |
| 2^3A_1 | 6.54×10^{-5} | 3.31×10^{-1} | | | | | |
| 1^3A_2 | — | — | 3.32×10^{-1} | | | | |
| 1^3B_2 | — | — | — | 3.32×10^{-1} | | | |
| 2^3B_2 | — | — | — | -1.69×10^{-2} | 3.31×10^{-1} | | |
| 3^3B_2 | — | — | — | -4.34×10^{-3} | -5.15×10^{-3} | 3.32×10^{-1} | |
| Hamiltonian | | | | | | | |
| 1^3A_1 | -1.03×10^2 | | | | | | |
| 2^3A_1 | -2.01×10^{-2} | -1.03×10^2 | | | | | |
| 1^3A_2 | — | — | -1.03×10^2 | | | | |
| 1^3B_2 | — | — | — | -1.03×10^2 | | | |
| 2^3B_2 | — | — | — | 5.26×10^0 | -1.03×10^2 | | |
| 3^3B_2 | — | — | — | 1.35×10^0 | 1.60×10^0 | -1.03×10^2 | |