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Local CC2 response method based on the Laplace transform: Orbital-relaxed first-order properties for excited states

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A multistate local CC2 response method for the calculation of orbital-relaxed first order properties is presented for ground and electronically excited states. It enables the treatment of excited state properties including orbital relaxation for extended molecular systems and is a major step on the way towards analytic gradients with respect to nuclear displacements. The Laplace transform method is employed to partition the eigenvalue problem and the lambda equations, i.e., the doubles parts of these equations are inverted on-the-fly, leaving only the corresponding effective singles equations to be solved iteratively. Furthermore, the state specific local approximations are adaptive. Density-fitting is utilized to decompose the electron-repulsion integrals. The accuracy of the local approximation is tested and the efficiency of the new code is demonstrated on the example of an organic sensitizer for solar-cell applications, which consists of about 100 atoms. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4818586]

I. INTRODUCTION

Electronically excited states play an important role in various scientific fields like biochemistry or material science, yet theoretical studies at a reliable level of *ab initio* theory are still very challenging. Time-dependent (TD) response theory is a widely used and general framework providing access to excitation energies and other properties of excited states for various wavefunction approaches: excitation energies are obtained as a property of the electronic ground state, namely, as the poles of the frequency-dependent polarizability (FDP). The use of TD response theory is well established, e.g., in the context of Hartree-Fock (TD-HF), density functional (TD-DFT),[1,2] or "traditional" Coupled Cluster theory (TD-CC).[3–6] Quite recently, also TD response methods for non-conventional, variational Coupled Cluster ansätze have been discussed.[7,8] In the following we focus on TD response of "traditional" Coupled Cluster theory. Here, the CC wavefunction ansatz is non-variational, implying that first an appropriate time-averaged quasienergy Lagrangian has to be specified,[9–11] from which then the linear response function, i.e., the FDP, is obtained by differentiation (rather than from the time-averaged quasienergy itself, as for variational methods). Note that the equation-of-motion Coupled Cluster (EOM-CC) method,[12–16] which approaches excited states from quite a different perspective, nevertheless has close relationships to TD-CC response; the excitation energies and relaxed densities of TD-CC response and EOM-CC are equivalent.

There is a hierarchy of CC models employed in the context of TD-CC response, differing in the level of truncation of the cluster operator, and in simplifications made in the CC amplitude equations based on many-body perturbation theory.[17] The computationally cheapest model of this hierarchy, which does not neglect dynamical correlation effects, is the CC2 model:[18] amplitudes related to double substitutions are correct only to first order (with respect to a Møller-Plesset (MP) partitioning of the Hamiltonian), yet the full $\exp(\mathbf{T_1})$ part of the CC ansatz is retained to provide partial orbital relaxation. The latter is important due to the neglect of explicit orbital relaxation in the (time-averaged) Lagrangian, which otherwise would cause fictitious additional poles originating from the underlying time-dependent Hartree-Fock solution.[6] The CC2 model provides rather accurate results for excited states, provided that they are dominated by singles substitutions.

First-order properties of individual excited states are, in the framework of TD-CC response, obtained as the derivatives (with respect to the strength of a time-independent perturbation) of the corresponding time-independent excited state Lagrangians involving the total energy of the related excited state, i.e., ground-state energy plus corresponding excitation energy.[6] For orbital-relaxed properties these Lagrangians are augmented by additional conditions related to the orbitals, such as the Brillouin condition.

Compared to computationally cheap methods like TD-DFT, canonical TD-CC methods have the disadvantage of a rather steep scaling of the computational cost with molecular size $\mathcal{N}$, e.g., canonical TD-CC2 scales as $\mathcal{O}(\mathcal{N}^5)$. Therefore, for extended molecular systems TD-DFT might be the sole applicable method, although it is unreliable and often fails qualitatively, if charge transfer states, Rydberg states, or excitations of extended π systems are involved.[2,19,20] In order to reduce the computational cost of TD-CC density

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fitting (DF)[21–23] can be employed, which factorizes the electron repulsion integrals. There are highly efficient CC2 and scaled opposite-spin (SOS) CC2 implementations using this approach for excited states.[24–29] However, DF reduces only the prefactor, but not the scaling: DF-CC2 still scales as $\mathcal{O}(\mathcal{N}^5)$, the approximate DF-SOS-CC2 method as $\mathcal{O}(\mathcal{N}^4)$.

In order to reduce the scaling further local correlation methods have been proposed.[30–34] The idea is to take advantage of the short-range nature of dynamic correlation in nonmetallic systems. To this end a basis of spatially localized orbitals, e.g., localized molecular orbitals (LMOs) and projected atomic orbitals (PAOs) is used to span occupied and virtual space, respectively.[35,36] Both the LMO pair list and the (pair specific) virtual spaces can then be restricted, the latter to subspaces of PAOs (domains). To specify such restrictions *a priori* is rather straightforward for calculations of the ground state amplitudes, but more intricate for eigenvectors of excited states.[30,32,37,38] For example, a certain eigenvector may want to change in the course of the iterative Davidson diagonalization and acquire Rydberg or charge transfer character, if the virtual space allows for it.

In the local CC2 response method based on the Laplace transform, denoted as LT-DF-LCC2, the eigenvalue problem, which determines the excitation energies and the corresponding eigenvectors, can be partitioned by virtue of the Laplace transform trick along the doubles-doubles-block like in the canonical basis without losing the sparsity of the quantities in local basis.[32–34] Hence, as in the canonical case, just an effective eigenvalue problem in the space of the un-truncated singles determinants has to be solved, and the state specific local approximations imposed on the doubles part of the eigenvector do not enter the Davidson diagonalization explicitly. State specific restricted pair-lists and PAO domains for the doubles part are re-specified in every Davidson-refresh by analysis of the un-truncated doubles part of the actual approximation to the eigenvector related to diagonal pairs. If two states come energetically close, the local approximations of these states are unified. In contrast to previous local CC2 response methods,[30,31] the LT-DF-LCC2 method therefore is a multistate method in the same sense as canonical CC2 is.

LT-DF-LCC2 excitation energies, transition moments, and orbital-unrelaxed properties were implemented into the MOLPRO program package[39] and enable calculations for extended molecular systems consisting of hundred or more atoms.[32–34] In the present work the method is extended in so far that the orbitals are allowed to relax with respect to the perturbation, i.e., orbital-relaxed first-order properties for the LT-DF-LCC2 method are presented. This is a major step on the way to analytic gradients with respect to nuclear displacements for excited states.

This paper is organized as follows: First, the working equations for the implementation of orbital-relaxed properties of the ground and singlet and triplet excited states are derived (Sec. II). The accuracy of the local approximations is then explored and the efficiency of the new code is demonstrated on the example of 3-(5-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophene-2-yl)thiophene-2-yl)-2-cyanoacrylic acid, an organic sensitizer for solar-cell applications (Sec. III).

II. THEORY

In the following we employ the Einstein convention, i.e., repeated indices are implicitly summed up; summations are only written explicitly, if it is necessary for clarity. The formalism is derived for an orthonormal basis of molecular orbitals (MOs) and the transformation to the basis of nonorthogonal PAOs is performed *a posteriori*, as done in an earlier paper on the LMP2 gradient.[40] The MOs are expanded in an AO-basis χ_μ with metric $S_{\mu\nu}^{\text{AO}} = \langle \chi_\mu | \chi_\nu \rangle$,

$$\phi_p = \chi_\mu C_{\mu p}. \tag{1}$$

The composite coefficient matrix $\mathbf{C} = (\mathbf{L}|\mathbf{C^v})$ above concatenates the LMO coefficient matrix $\mathbf{L}$ and the coefficient matrix of the canonical virtuals $\mathbf{C^v}$. For LMOs and canonical virtuals we use indices $i, j, \ldots$, and $a, b, \ldots$, respectively. General molecular orbitals are indexed by $m, n, \ldots$, and PAOs by $r, s, \ldots$. The coefficient matrix $\mathbf{P}$ for the PAOs is given by

$$P_{\mu r} = [\mathbf{C^v C^{v\dagger} S^{AO}}]_{\mu r} = [\mathbf{C^v Q}]_{\mu r}, \tag{2}$$

implicitly defining the matrix $\mathbf{Q}$, which transforms from canonical to PAO basis. For the metric $\mathbf{S}$ of the PAOs one then obtains

$$\mathbf{S} = \mathbf{P^\dagger S^{AO} P} = \mathbf{Q^\dagger Q}. \tag{3}$$

In order to reduce the computational cost density fitting[21–23] is employed to decompose the four-index integrals into three-index objects, i.e.,

$$(mn|pq) \approx (mn|P)c_{pq}^P, \qquad c_{pq}^P = (J^{-1})_{PQ}(Q|pq), \tag{4}$$

with capital letters P, Q indexing the auxiliary fitting functions. $J_{PQ} = (P|Q)$ is an element of the Coulomb matrix of the auxiliary fitting functions.

A. Ground state

The CC2 model was proposed by Christiansen *et al.*[18] as an approximation to the CC singles and doubles (CCSD) model. The CC2 energy is usually calculated as

$$E_0 = \langle 0|\exp(-\mathbf{T})\mathbf{H}\exp(\mathbf{T})|0\rangle$$
$$= \langle 0|\hat{\mathbf{H}} + [\hat{\mathbf{H}}, \mathbf{T_2}]|0\rangle, \tag{5}$$

where $|0\rangle$ is the Hartree-Fock reference determinant, $\mathbf{H}$ is the Hamiltonian, and $\mathbf{T}$ is the cluster operator containing single and double excitations, i.e.,

$$\mathbf{T} = \mathbf{T_1} + \mathbf{T_2} = t_{\mu_1}\tau_{\mu_1} + t_{\mu_2}\tau_{\mu_2} = t_a^i \tau_i^a + t_{ab}^{ij}\tau_{ij}^{ab}, \tag{6}$$

with excitation operators τ and related amplitudes t. For singlet substitutions, as they occur for the electronic ground state and singlet excited states, τ is defined as

$$\tau_i^a = a_{a\alpha}^\dagger a_{i\alpha} + a_{a\beta}^\dagger a_{i\beta},$$
$$\tau_{ij}^{ab} = \frac{1}{2}(a_{a\alpha}^\dagger a_{i\alpha} + a_{a\beta}^\dagger a_{i\beta})(a_{b\alpha}^\dagger a_{j\alpha} + a_{b\beta}^\dagger a_{j\beta}), \tag{7}$$

in terms of the elementary second quantization creation and annihilation operators $a^\dagger$ and a (the compound index $i\alpha$ denotes a spin orbital related to a spatial LMO i times spin function α, *etc.*). Operators decorated by a hat represent operators

similarity transformed with the exponent of the singles cluster operator $\mathbf{T_1}$, e.g., $\hat{\mathbf{H}} = \exp(-\mathbf{T_1})\mathbf{H}\exp(\mathbf{T_1})$.

The CC2 amplitudes are determined by the equations

$$\Omega_{\mu_1} = \langle \tilde{\mu}_1 | \hat{\mathbf{H}} + [\hat{\mathbf{H}}, \mathbf{T_2}]|0\rangle = 0,$$
$$\Omega_{\mu_2} = \langle \tilde{\mu}_2 | \hat{\mathbf{H}} + [\mathbf{F} + \hat{\mathbf{V}}_0, \mathbf{T_2}]|0\rangle = 0. \tag{8}$$

$\langle \tilde{\mu}_1|$ and $\langle \tilde{\mu}_2|$ are contravariant configuration state functions projecting onto the singles and doubles manifold,[41] $\mathbf{F}$ is the Fock operator, and $\mathbf{V_0}$ a time-independent perturbation, which is already included in $\mathbf{H}$, e.g., an applied electric field. It consists of a Hermitian perturbation operator $\mathbf{X}$ describing the observable and the corresponding perturbation strength ϵ_X,

$$\mathbf{V_0} = \sum_X \epsilon_X \mathbf{X} = \sum_{pq} [\mathbf{v_0}]_{pq} \tau_q^p, \tag{9}$$

with the matrix elements

$$[\mathbf{v_0}]_{pq} = \sum_X X_{pq} \epsilon_X. \tag{10}$$

A consequence of the similarity transformed operators is the occurrence of *dressed* integrals,

$$(mn\hat{|}pq) = (\mu\nu|\rho\sigma)\Lambda_{\mu m}^p \Lambda_{\nu n}^h \Lambda_{\rho p}^p \Lambda_{\sigma q}^h, \tag{11}$$

with the coefficient matrices $\mathbf{\Lambda^p}$ and $\mathbf{\Lambda^h}$ in LMO/PAO-basis defined as

$$\Lambda_{\mu r}^p = P_{\mu r} - L_{\mu i} t_{r'}^i S_{r'r}, \quad \Lambda_{\mu i}^p = L_{\mu i},$$
$$\Lambda_{\mu r}^h = P_{\mu r}, \quad\quad\quad\quad \Lambda_{\mu i}^h = L_{\mu i} + P_{\mu r} t_r^i. \tag{12}$$

For the Fock matrix internal and external dressing is distinguished. *Internal dressing* refers to the use of the coefficient matrices $\mathbf{\Lambda^p}$ and $\mathbf{\Lambda^h}$ in the contraction with the four-index integrals *inside* the Fock matrix,

$$\hat{f}_{\mu\nu} = h_{\mu\nu} + 2\Lambda_{\rho k}^p \Lambda_{\sigma k}^h \left[(\mu\nu|\rho\sigma) - \frac{1}{2}(\mu\rho|\sigma\nu) \right]. \tag{13}$$

Internal dressing actually involves contractions with the fluctuation potential (evident, when the $\exp(-\mathbf{T_1})\mathbf{H}\exp(\mathbf{T_1})$ transformation is carried out *after* $\mathbf{H}$ is written in normal ordered form) and is therefore of first-order. *External dressing*, on the other hand, means the use of these coefficient matrices for the transformation of the Fock matrix to the MO basis and is of zeroth-order.

In this paper, dressed integrals and other objects containing such integrals are decorated by a hat. If not explicitly stated otherwise, $\hat{f}_{pq}$ implies internal and external dressing.

1. The orbital-unrelaxed Lagrangian

The general local CC2 Lagrangian for the electronic ground state without orbital relaxation, which was also used in previous work,[31,33,34] reads

$$\mathcal{L}_0' = E_0 + \tilde{\lambda}_{\mu_i}^0 \Omega_{\mu_i}. \tag{14}$$

It includes the ground state energy E_0 and the amplitude equations $\mathbf{\Omega}$. The Lagrangian is required to be stationary with respect to all parameters. Differentiation of $\mathcal{L}_0'$ with respect to

the amplitudes t yields the equations for the multipliers $\tilde{\lambda}^0$, i.e., the lambda equations

$$-\eta_{\nu_j} = \tilde{\lambda}_{\mu_i}^0 A_{\mu_i \nu_j}, \tag{15}$$

with the Jacobian

$$A_{\mu_i \nu_j} = \frac{\partial \Omega_{\mu_i}}{\partial t_{\nu_j}} \tag{16}$$

and

$$\eta_{\nu_j} = \frac{\partial E_0}{\partial t_{\nu_j}}. \tag{17}$$

Laplace transform is used to partition the $\tilde{\lambda}^0$ equation system (15) such that an effective equation system for only the singles part has to be solved, similarly as it is done for properties of excited states (cf. Sec. II.B.1 in Ref. 34). This effective singles equation system,

$$-\eta_{\mu_1} = \tilde{\lambda}_{\nu_1}^0 A_{\nu_1 \mu_1} + \tilde{\lambda}_{\nu_2}^0 (\tilde{\lambda}_{\nu_1}^0) A_{\nu_2 \mu_1}, \tag{18}$$

contains the quantity

$$\lambda_{\nu_2}^0 (\tilde{\lambda}_{\nu_1}^0) = {}^{I}\lambda_{\nu_2}^0 (\tilde{\lambda}_{\nu_1}^0) + {}^{II}\lambda_{\nu_2}^0. \tag{19}$$

The $\tilde{\lambda}_\mu^0$ are the contravariant ground-state multipliers, i.e.,

$$\tilde{\lambda}_r^i = \frac{1}{2}\lambda_r^i \quad \text{and} \quad \tilde{\lambda}_{rs}^{ij} = 2\lambda_{rs}^{ij} - \lambda_{rs}^{ji}. \tag{20}$$

${}^{I}\lambda_{\nu_2}^0 (\tilde{\lambda}_{\nu_1}^0)$ in (19) depends on $\tilde{\lambda}_{\nu_1}^0$, whereas ${}^{II}\lambda_{\nu_2}^0$, which is originating from the l.h.s. η, is independent of $\tilde{\lambda}_{\nu_1}^0$ (cf. Eq. (34) in Ref. 34 and the preceding discussion therein). ${}^{I}\lambda_{\nu_2}^0 (\tilde{\lambda}_{\nu_1}^0)$ is identical to the corresponding quantity for excited states (cf. Eq. (38) in Ref. 34) after replacing the excited state multipliers $\tilde{\lambda}^f$ by $\tilde{\lambda}^0$. The quantity ${}^{II}\lambda_{\nu_2}^0$ reads

$$
{}^{II}\lambda_{rs}^{ij} = -V_{rt}^{ij} V_{su}^{ij} \frac{(1 + \mathcal{P}_{ij}\mathcal{P}_{tu})}{2} \sum_{q=1}^{n_q} \text{sgn}(w_q)
$$
$$
\times X_{tv'}^v(q) V_{v'v}^\dagger X_{uw'}^v(q) V_{w'w}^\dagger (kv|P) c_{lw}^P X_{ki}^o(q) X_{lj}^o(q), \tag{21}
$$

with the permutation operator $\mathcal{P}_{pq}$,

$$\mathcal{P}_{pq} X_{pq} = X_{qp}, \tag{22}$$

the Laplace quadrature points t_q, their weights w_q, and the matrices $\mathbf{X}^v(q)$ and $\mathbf{X}^o(q)$,

$$X_{ij}^o(q) = W_{\bar{i}i}^\dagger e^{(\epsilon_{\bar{i}} - \epsilon_F)t_q + \frac{1}{4}\ln(|w_q|)} W_{\bar{i}j},$$
$$X_{rs}^v(q) = Q_{ra}^\dagger e^{(-\epsilon_a + \epsilon_F)t_q + \frac{1}{4}\ln(|w_q|)} Q_{as}. \tag{23}$$

The matrix $\mathbf{W}$ transforms canonical occupied orbitals $(\bar{i}, \bar{j}, \ldots)$ to LMOs $(i, j, \ldots)$. The matrix $\mathbf{V}$ is a pseudo-inverse of the PAO metric $\mathbf{S}$. When local approximations are invoked, $\mathbf{V}$ is the pseudo-inverse of the corresponding block of the PAO metric and thus may be pair-specific. This pair specificity of the pseudoinverse is explicitly indicated in Eq. (21) and it is understood that the summation does not run over the repeated indices i, j. ϵ_p is the energy of orbital p and $\epsilon_F = (\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}})/2$ ensures that the individual exponential factors are always smaller than one (for positive t_q). A detailed derivation

and discussion of the Laplace transformation matrices in Eq. (23) can be found in Ref. 48.

2. Including orbital relaxation

The general local CC2 Lagrangian for the electronic ground state including orbital relaxation reads

$$\mathcal{L}_0 = \mathcal{L}_0' + z_{ij}^{loc,0} r_{ij} + z_{ai}^0 [\mathbf{f} + \mathbf{v_0}]_{ai}$$
$$+ x_{pq}^0 [\mathbf{C}^\dagger \mathbf{S}^{AO} \mathbf{C} - \mathbf{1}]_{pq}, \quad (24)$$

where $[\mathbf{f} + \mathbf{v_0}]_{ai}$ are the occupied-virtual matrix elements of the perturbed Fock operator $[\mathbf{F} + \mathbf{V_0}]$. Compared to the orbital-unrelaxed Lagrangian $\mathcal{L}_0'$, $\mathcal{L}_0$ contains further conditions, namely, localization, Brillouin, and orthonormality conditions. The related multipliers are $z_{ij}^{loc,0}$, z_{ai}^0, and x_{pq}^0, respectively. Note that the multipliers x_{pq}^0 related to the orthogonality condition are redundant, since $\mathbf{x^0} = \mathbf{x^{0\dagger}}$. This will be resolved later. By choosing Pipek-Mezey localization[42] the conditions r_{ij} become

$$r_{ij} = \sum_A \left[S_{ii}^A - S_{jj}^A \right] S_{ij}^A = 0 \quad \text{for all} \quad i > j, \quad (25)$$

with the matrix $\mathbf{S^A}$ being defined as

$$S_{kl}^A = \sum_{\mu \in A} \sum_\nu \left[L_{\mu k} S_{\mu\nu}^{AO} L_{\nu l} + L_{\mu l} S_{\mu\nu}^{AO} L_{\nu k} \right]. \quad (26)$$

The summation over μ is restricted to basis functions centered on atom A. Differentiation of $\mathcal{L}_0$ with respect to orbital variations yields the *z-vector equations*, from which the multipliers $\mathbf{z^0}$, $\mathbf{z^{loc,0}}$, and $\mathbf{x^0}$ are obtained (*vide infra*).[40] Differentiation with respect to the strength ϵ_X of the perturbation $\mathbf{V_0}$ finally yields the orbital-relaxed property $\langle X \rangle_0^{rel}$, e.g., the orbital-relaxed dipole moment in case of an electric field, which generally can be written as the trace of density matrix, backtransformed to AO basis, with the integrals $X_{\mu\nu}^{AO} = \langle \chi_\mu | \mathbf{X} | \chi_\nu \rangle$ representing the operator $\mathbf{X}$ in the AO basis, i.e., as

$$\langle X \rangle_0^{rel} = \text{tr} \left[\mathbf{X}^{AO} \left(\mathcal{D}_{AO}^0 + z_{AO}^0 \right) \right]. \quad (27)$$

z_{AO}^0 are the multipliers for the Brillouin condition transformed to AO basis and the explicit form of the density $\mathcal{D}_{AO}^0$ is derived in Sec. II D.

The derivation of the *z-vector equations* for the multipliers $\mathbf{z^0}$, $\mathbf{z^{loc,0}}$, and $\mathbf{x^0}$ proceeds in an analogous way as for the LMP2 gradient:[40,43] the variations of the orbitals in the presence of the perturbation $\mathbf{V_0}$ are described by the coefficient matrix

$$C_{\mu p}(\mathbf{V_0}) = C_{\mu q}(0) O_{qp}(\mathbf{V_0}), \quad (28)$$

where $\mathbf{C(0)}$ are the coefficients of the optimized orbitals without perturbation and the matrix $\mathbf{O(V_0)}$ describes the rotation of the orbitals caused by $\mathbf{V_0}$, with $\mathbf{O(0)} = \mathbf{1}$.

The derivative of the Lagrangian with respect to the variation can be partitioned into four contributions,

$$\left(\frac{\partial \mathcal{L}_0}{\partial O_{pq}} \right)_{\mathbf{V}=0} = [\mathbf{B^0} + \tilde{\mathbf{B}}(\mathbf{z^0}) + \mathbf{b}(\mathbf{z^{loc,0}}) + 2\mathbf{x^0}]_{pq}, \quad (29)$$

with

$$[\mathbf{B^0}]_{pq} = \left(\frac{\partial}{\partial O_{pq}} \mathcal{L}_0' \right)_{\mathbf{V}=0},$$

$$[\tilde{\mathbf{B}}(\mathbf{z^0})]_{pq} = \left(\frac{\partial}{\partial O_{pq}} z_{ai}^0 f_{ai} \right)_{\mathbf{V}=0}, \quad (30)$$

$$[\mathbf{b}(\mathbf{z^{loc,0}})]_{pi} = \left(\frac{\partial}{\partial O_{pi}} z_{kl}^{loc,0} r_{kl} \right)_{\mathbf{V}=0}.$$

$\mathbf{B^0}$, $\tilde{\mathbf{B}}(\mathbf{z^0})$, and $\mathbf{b}(\mathbf{z^{loc,0}})$ were denoted as $\mathbf{A}$, $\tilde{\mathbf{A}}$, and $\mathbf{a}(\mathbf{z^{loc}})$, respectively, in Ref. 40, but in this publication $\mathbf{A}$ is already reserved for the CC2 Jacobian (cf. Sec. II B). The stationarity of $\mathcal{L}_0$ with respect to orbital variations, and the relation $\mathbf{x^0} = \mathbf{x^{0\dagger}}$ are exploited to obtain the linear *z-vector equations*,

$$(1 - \mathcal{P}_{pq})[\mathbf{B^0} + \tilde{\mathbf{B}}(\mathbf{z^0}) + \mathbf{b}(\mathbf{z^{loc,0}})]_{pq} = 0, \quad (31)$$

from which $\mathbf{z^0}$ and $\mathbf{z^{loc,0}}$ are obtained. The matrix $\mathbf{x^0}$, which is only needed for the gradient with respect to nuclear displacements, i.e., when the basis functions are affected by $\mathbf{V_0}$, can then be expressed as

$$x_{pq}^0 = -\frac{1}{4}(1 + \mathcal{P}_{pq})[\mathbf{B^0} + \tilde{\mathbf{B}}(\mathbf{z^0}) + \mathbf{b}(\mathbf{z^{loc,0}})]_{pq}. \quad (32)$$

As shown in Ref. 40, the *z-vector equations* (31) can be further decoupled into the Z-CPL (coupled perturbed localization), and the Z-CPHF (coupled perturbed Hartree-Fock) equations. The former have to be solved first, since the solutions of the Z-CPL equations, the $\mathbf{z^{loc,0}}$, do appear in the Z-CPHF equations, which, in turn, determine the $\mathbf{z^0}$ multipliers.

The quantities $\tilde{\mathbf{B}}(\mathbf{z^0})$ and $\mathbf{b}(\mathbf{z^{loc,0}})$ appearing in Eqs. (31) and (32) are identical to the quantities $\tilde{\mathbf{A}}$ and $\mathbf{a}(\mathbf{z^{loc}})$ given explicitly in Eqs. (29) and (39), respectively, of Ref. 40. For the quantity $\mathbf{B^0}$ one obtains after differentiation according to Eq. (30)

$$B_{pq}^0 = C_{\mu p} B_{\mu i}^0 + C_{\mu p} B_{\mu r}^0 Q_{ra} + C_{\mu p} S_{\mu\rho}^{AO} \delta_{\rho r} B_{rv}^0 C_{va}^v, \quad (33)$$

where the intermediates $B_{\mu i}^0$ and $B_{\mu r}^0$ are simply the partial derivatives of $\mathcal{L}_0'$ with respect to O_{pq} for $q = i$ and $q = r$, respectively. The third term involving B_{rv}^0 originates from the dependence of the multipliers and amplitudes in the local basis on the coefficients $\mathbf{C}$ via the transformation matrix $\mathbf{Q} = \mathbf{C^{v\dagger} S^{AO}}$, i.e.,

$$C_{\mu p} S_{\mu\rho}^{AO} \delta_{\rho r} B_{rv}^0 C_{va}^v = \sum_{\mu_i} \left[\left(\frac{\partial \mathcal{L}_0'}{\partial \tilde{\lambda}_{\mu_i}^0} \right) \left(\frac{\partial \tilde{\lambda}_{\mu_i}^0}{\partial O_{pq}} \right) \right]_{\mathbf{V}=0}$$
$$+ \sum_{\mu_i} \left[\left(\frac{\partial \mathcal{L}_0'}{\partial t_{\mu_i}} \right) \left(\frac{\partial t_{\mu_i}}{\partial O_{pq}} \right) \right]_{\mathbf{V}=0}, \quad (34)$$

with $\tilde{\lambda}_{\mu_i}^0$ and t_{μ_i} representing zeroth order multipliers and ground state amplitudes related to singles ($i = 1$) and doubles ($i = 2$) substitutions, respectively, in local occupied and canonical virtual orbital basis, e.g., $t_{\mu_2} \equiv t_{ab}^{ij}$. The derivatives with respect to multipliers and amplitudes in Eq. (34) vanish only for the singles substitutions, which are not restricted to domains. The working equations for the $B_{\mu i}^0$, $B_{\mu r}^0$, and B_{rv}^0 are derived in Appendix A.

B. Singlet excited states

Details about the calculation of excited state properties without orbital relaxation using the LT-DF-LCC2 method were presented earlier.[33,34] To obtain excitation energies and properties of an excited state f the left and right eigenvalue equations for the Jacobian $\mathbf{A}$,

$$\mathbf{A}R^f = \omega_f \mathbf{M}R^f \quad \text{and} \quad \tilde{L}^f \mathbf{A} = \omega_f \tilde{L}^f \mathbf{M}, \tag{35}$$

have to be solved to obtain the contravariant left eigenvector $\tilde{L}^f$ and the covariant right eigenvector R^f (the matrix $\mathbf{M}$ is their metric). The resulting eigenvalues ω are the excitation energies of the system. The CC2 Jacobian for singlet states takes the form

$$A_{\mu_i \nu_j} = \begin{pmatrix} \langle \tilde{\mu}_1 | [\hat{\mathbf{H}}, \tau_{\nu_1}](1+\mathbf{T_2})|0\rangle & \langle \tilde{\mu}_1 | [\hat{\mathbf{H}}, \tau_{\nu_2}]|0\rangle \\ \langle \tilde{\mu}_2 | [\hat{\mathbf{H}}, \tau_{\nu_1}]|0\rangle & \langle \tilde{\mu}_2 | [\mathbf{F} + \hat{\mathbf{V}_0}, \tau_{\nu_2}]|0\rangle \end{pmatrix}, \tag{36}$$

and the local CC2 Lagrangian for excited states including orbital relaxation can be expressed as

$$\mathcal{L}_{f'} = E_0 + \tilde{L}^f \mathbf{A} R^f + \tilde{\lambda}_{\mu_i}^{f'} \Omega_{\mu_i}$$
$$- \omega_f [\tilde{L}^f \mathbf{M} R^f - 1] + z_{ij}^{loc,f'} r_{ij}$$
$$+ z_{ai}^{f'} [\mathbf{f} + \mathbf{v_0}]_{ai} + x_{pq}^{f'} [\mathbf{C}^\dagger \mathbf{S}^{AO} \mathbf{C} - 1]_{pq}. \tag{37}$$

The sum of the first two terms represents the energy of the excited state f, the third term is the condition for the ground state amplitudes. The fourth term enforces the orthogonality of left and right eigenvector and the remaining terms represent the localization, Brillouin, and orbital-orthogonality conditions, respectively. The ground state quantities are calculated only once in the beginning, thus only the difference to the ground state ($\mathcal{L}_f = \mathcal{L}_{f'} - \mathcal{L}_0$) has to be considered for the excited states. The corresponding Lagrange multipliers are defined as

$$\tilde{\lambda}^f = \tilde{\lambda}^{f'} - \tilde{\lambda}^0, \qquad x^f = x^{f'} - x^0,$$
$$z^f = z^{f'} - z^0, \qquad z^{loc,f} = z^{loc,f'} - z^{loc,0}. \tag{38}$$

For the sake of clarity the state index f is omitted for L, R, and ω in the following. Differentiation of the Lagrangian $\mathcal{L}_f$ with respect to the amplitudes t yields the equation for the multipliers $\tilde{\lambda}^f$, for the working equations we refer to Ref. 33. Furthermore, analogously to the ground state, stationarity of $\mathcal{L}_f$ with respect to orbital variations, i.e.,

$$0 = \left(\frac{\partial}{\partial O_{pq}} \left[\tilde{L}\mathbf{A}R + \tilde{\lambda}_{\mu_i}^f \Omega_{\mu_i} - \omega[\tilde{L}\mathbf{M}R - 1] \right. \right.$$
$$+ z_{ij}^{loc,f} r_{ij} + z_{ai}^f [\mathbf{f} + \mathbf{v_0}]_{ai}$$
$$\left. \left. + x_{pq}^f [\mathbf{C}^\dagger \mathbf{S}\mathbf{C} - 1]_{pq} \right] \right)_{\mathbf{V}=0}, \tag{39}$$

yields the *z-vector equations*,

$$0 = (1 - \mathcal{P}_{pq})[\mathbf{B^f} + \tilde{\mathbf{B}}(\mathbf{z^f}) + \mathbf{b}(\mathbf{z^{loc,f}})]_{pq}, \tag{40}$$

which corresponds to Eq. (31) for the ground state, and a set of equations corresponding to Eq. (32). Equation (40) again decouples in the Z-CPL equations determining $\mathbf{z^{loc,f}}$, and the Z-CPHF equations determining $\mathbf{z^f}$. Apart from a different right-

hand side these equations are equivalent to those of the ground state. In Eq. (40) the quantities $\tilde{\mathbf{B}}(\mathbf{z^f})$ and $\mathbf{b}(\mathbf{z^{loc,f}})$ are defined according to Eq. (30), and

$$B_{pq}^f = \left(\frac{\partial}{\partial O_{pq}} (\tilde{L}\mathbf{A}R + \tilde{\lambda}_{\mu i}^f \Omega_{\mu i} - \omega(\tilde{L}\mathbf{M}R - 1)) \right)_{\mathbf{V}=0}$$
$$= C_{\mu p} B_{\mu i}^f + C_{\mu p} B_{\mu r}^f Q_{ra} + C_{\mu p} S_{\mu \rho}^{AO} \delta_{\rho r} B_{r\nu}^f C_{\nu a}^v. \tag{41}$$

The working equations for the intermediates $B_{\mu i}^f$, $B_{\mu r}^f$, and $B_{r\nu}^f$ in local basis are provided in Appendix B. Analogously to the ground state, $B_{\mu i}^f$ and $B_{\mu r}^f$ are the direct partial derivatives with respect to O_{pq} for $q = i$ and $q = r$, respectively. The term including $B_{r\nu}^f$ arises from the dependence of the doubles amplitudes, eigenvectors, and Lagrange multipliers on the orbital variation (cf. Eq. (34) for the ground state case).

Orbital-relaxed properties, e.g., the dipole moment, are obtained by differentiation of the Lagrangian $\mathcal{L}_{f'}$ with respect to the perturbation strength ϵ_x, yielding

$$\langle X \rangle_{f'}^{rel} = \langle X \rangle_0^{rel} + \langle X \rangle_f^{rel}, \quad \text{with}$$
$$\langle X \rangle_f^{rel} = \tilde{\lambda}^f \xi^X + \tilde{L}\mathbf{A}^\mathbf{X}R + z_{ai}^f X_{ai} \tag{42}$$
$$= \mathrm{tr} \left[\mathbf{X}^{AO} \left(\mathcal{D}_{AO}^f + z_{AO}^f \right) \right],$$

$$A_{\mu_i \nu_j}^X = \frac{\partial A_{\mu_i \nu_j}}{\partial \epsilon_X}, \quad \text{and} \quad \xi_{\mu_i}^X = \frac{\partial \Omega_{\mu_i}}{\partial \epsilon_X}. \tag{43}$$

$\langle X \rangle_0^{rel}$ is calculated according to Eq. (27), and the explicit expression for the density $\mathcal{D}_{AO}^f$ is given in Sec. II D.

C. Triplet excited states

Triplet states for canonical CC2 response were introduced in Ref. 26, and later also implemented in the framework of the LT-DF-LCC2 method.[34] For triplet substitutions the excitation operators τ are defined as

$$\tau_i^a = a_{a\alpha}^\dagger a_{i\alpha} - a_{a\beta}^\dagger a_{i\beta},$$
$$\tau_{ij}^{ab} = (a_{a\alpha}^\dagger a_{i\alpha} - a_{a\beta}^\dagger a_{i\beta})(a_{b\alpha}^\dagger a_{j\alpha} + a_{b\beta}^\dagger a_{j\beta}). \tag{44}$$

Contrary to the singlet case the triplet double substitution operators have no permutational symmetry ($\tau_{ij}^{ab} \neq \tau_{ji}^{ba}$), but they are linearly dependent according to

$$\tau_{ij}^{ab} + \tau_{ji}^{ba} + \tau_{ij}^{ab} + \tau_{ji}^{ba} = 0. \tag{45}$$

To get rid of these redundancies symmetrized operators of the form

$$\overset{(+)}{\tau_{ij}^{ab}} = \tau_{ij}^{ab} + \tau_{ji}^{ba}, \quad \forall a > b, i > j \text{ and}$$
$$\overset{(-)}{\tau_{ij}^{ab}} = \tau_{ij}^{ab} - \tau_{ji}^{ba}, \quad \forall (ai) > (bj) \tag{46}$$

are introduced, which fulfill the symmetry relations

$$\overset{(+)}{\tau_{ij}^{ab}} = \overset{(+)}{\tau_{ji}^{ba}} = -\overset{(+)}{\tau_{ij}^{ba}} = -\overset{(+)}{\tau_{ji}^{ab}},$$
$$\overset{(-)}{\tau_{ij}^{ab}} = -\overset{(-)}{\tau_{ji}^{ba}}. \tag{47}$$

Thus, symmetrized doubly excited `ket` and `bra` configuration state functions for triplet states are defined as

$$\left|\overset{(+)}{\Phi_{ij}^{ab}}\right\rangle = \overset{(+)}{\tau_{ij}^{ab}}|0\rangle, \qquad \left|\overset{(-)}{\Phi_{ij}^{ab}}\right\rangle = \overset{(-)}{\tau_{ij}^{ab}}|0\rangle,$$

$$\left\langle\overset{(+)}{\tilde{\Phi}_{ij}^{ab}}\right| = \frac{1}{8}\langle 0|\left(\overset{(+)}{\tau_{ij}^{ab}}\right)^{\dagger}, \qquad \left\langle\overset{(-)}{\tilde{\Phi}_{ij}^{ab}}\right| = \frac{1}{8}\langle 0|\left(\overset{(-)}{\tau_{ij}^{ab}}\right)^{\dagger}, \tag{48}$$

and triplet singles and doubles cluster operators $\mathbf{U_1}$ and $\mathbf{U_2}$ as

$$\mathbf{U_1} = \sum_{ia} u_a^i \tau_i^a,$$

$$\mathbf{U_2} = \sum_{a>b, i>j} \overset{(+)}{U_{ab}^{ij}}\overset{(+)}{\tau_{ij}^{ab}} + \sum_{(ai)>(bj)} \overset{(-)}{U_{ab}^{ij}}\overset{(-)}{\tau_{ij}^{ab}}. \tag{49}$$

The Jacobian $\mathbf{A}$ in Eq. (37) takes for triplet excited states the form

$$A_{\mu_i\nu_j} = \begin{pmatrix} \langle\tilde{\mu}_1|[\hat{\mathbf{H}}, \tau_{\nu_1}](1+\mathbf{T_2})|0\rangle & \langle\tilde{\mu}_1|[\hat{\mathbf{H}}, \overset{(+)}{\tau_{\nu_2}}]|0\rangle & \langle\tilde{\mu}_1|[\hat{\mathbf{H}}, \overset{(-)}{\tau_{\nu_2}}]|0\rangle \\ \langle\overset{(+)}{\tilde{\mu}_2}|[\hat{\mathbf{H}}, \tau_{\nu_1}]|0\rangle & \langle\overset{(+)}{\tilde{\mu}_2}|[\mathbf{F}+\hat{\mathbf{V}_0}, \overset{(+)}{\tau_{\nu_2}}]|0\rangle & 0 \\ \langle\overset{(-)}{\tilde{\mu}_2}|[\hat{\mathbf{H}}, \tau_{\nu_1}]|0\rangle & 0 & \langle\overset{(-)}{\tilde{\mu}_2}|[\mathbf{F}+\hat{\mathbf{V}_0}, \overset{(-)}{\tau_{\nu_2}}]|0\rangle \end{pmatrix}. \tag{50}$$

Recall that the cluster operator $\mathbf{T}$ refers to the ground state and therefore contains singlet excitation operators. First order orbital-relaxed properties are calculated according to Eq. (42), but with the corresponding density matrix $\mathcal{D}_{AO}^f$ for triplet states, which is given explicitly in Sec. II D.

The quantity $\mathbf{B^f}$ for the *z-vector equations* (Eq. (40)) is obtained according to Eq. (41) with intermediates $B_{\mu i}^f$, $B_{\mu r}^f$, and $B_{r\nu}^f$ as defined in Appendix C. The term including $B_{r\nu}^f$ again arises from the dependence of the doubles quantities on the orbital variation via the transformation matrix $\mathbf{Q}$, in analogy to Eq. (34) for the ground state case.

D. Orbital-relaxed densities

In the following the individual density matrices are given explicitly in the LMO/PAO basis, i.e., *after* transformation from canonical virtuals to PAOs.

For the orbital-relaxed case the term $\mathbf{F} + \hat{\mathbf{V}_0}$ in the commutator of the doubles amplitude equation Ω_{μ_2} (8) simplifies to $\mathbf{F} + \mathbf{V_0}$, i.e., the dressed time-independent perturbation has to be replaced by the undressed one. The reason for this is the explicit inclusion of the Brillouin condition in the Lagrangian (cf. Eqs. (24) and (37)). Consequently, the occupied-virtual matrix elements $[\mathbf{f} + \mathbf{v_0}]_{ia}$, which occur in the external dressing of the internal-internal and external-external blocks $[\hat{\mathbf{f}} + \hat{\mathbf{v}_0}]_{ij}$ and $[\hat{\mathbf{f}} + \hat{\mathbf{v}_0}]_{ab}$ in the commutator of the Ω_{μ_2} equation, are zero. Note that the related $\mathbf{F}$ operator is neither externally nor internally dressed (unlike the $\hat{\mathbf{F}}$ included in the operators $\hat{\mathbf{H}}$), since only the external dressing is of zeroth-order, while the internal dressing of $\hat{\mathbf{F}}$ is of first-order (*vide supra*) and therefore neglected in the CC2 Ω_{μ_2} equation.

Having $\mathbf{F} + \mathbf{V_0}$ instead of $\mathbf{F} + \hat{\mathbf{V}_0}$ in the Ω_{μ_2} equation implies that the density matrices are generally different to those of the orbital-unrelaxed case and consist of an "undressed" part $\mathcal{D}$, and a "dressed" part $\hat{\mathcal{D}}$. $\mathcal{D}$ originates from the term involving the bare $\mathbf{V_0}$ operator in the Ω_{μ_2}

condition of the Lagrangian and transforms to the AO basis via the ordinary LMO and PAO coefficient matrices $\mathbf{L}$ and $\mathbf{P}$, which are concatenated in the combined coefficient matrix $\mathbf{C^{loc}} = (\mathbf{L}|\mathbf{P})$. $\hat{\mathcal{D}}$, on the other hand, originates from the terms in the Lagrangian involving the similarity transformed $\hat{\mathbf{V}_0}$ (via $\hat{\mathbf{H}}$) and transforms to AO basis via the coefficient matrices $\mathbf{\Lambda^p}$ and $\mathbf{\Lambda^h}$ defined in Eq. (12). Hence, generally, the orbital-relaxed density matrices in AO basis $\mathcal{D}_{AO}$ are obtained as

$$\mathcal{D}_{\mu\nu} = C_{\mu p}^{loc}\mathcal{D}_{pq}C_{\nu q}^{loc} + \Lambda_{\mu p}^p\hat{\mathcal{D}}_{pq}\Lambda_{\nu q}^h. \tag{51}$$

In the orbital-unrelaxed case only the similarity transformed perturbation $\hat{\mathbf{V}_0}$ occurs and thus the first term in Eq. (51) is dropped.

The first density matrix $\mathcal{D}_{AO}^0$, needed for the evaluation of ground state properties $\langle X\rangle_0^{rel}$ according to Eq. (27), is calculated via (51) with

$$\mathcal{D}_{pq}^0 = 2(\delta_{pi}\delta_{qi} + \delta_{pr}\delta_{qi}t_r^i) + \mathcal{D}_{pq}^\xi(\lambda^0), \quad \hat{\mathcal{D}}_{pq}^0 = \hat{\mathcal{D}}_{pq}^\xi(\lambda^0),$$

$$\text{with} \quad \mathcal{D}_{ij}^\xi(\lambda^0) = -2\tilde{\lambda}_{rs'}^{jk,0}S_{r'r}t_{r's}^{ik}S_{s's},$$

$$\mathcal{D}_{rs}^\xi(\lambda^0) = 2\tilde{\lambda}_{st'}^{kl,0}S_{t't}t_{rt}^{kl},$$

$$\mathcal{D}_{ri}^\xi(\lambda^0) = \mathcal{D}_{ir}^\xi(\lambda^0) = 0, \tag{52}$$

$$\hat{\mathcal{D}}_{ir}^\xi(\lambda^0) = \tilde{\lambda}_r^{i,0},$$

$$\hat{\mathcal{D}}_{ri}^\xi(\lambda^0) = \tilde{\lambda}_{s'}^{k,0}S_{s's}\tilde{t}_{rs}^{ik},$$

$$\hat{\mathcal{D}}_{rs}^\xi(\lambda^0) = \hat{\mathcal{D}}_{ij}^\xi(\lambda^0) = 0.$$

In contrast, for the orbital-unrelaxed case, all submatrices of $\mathcal{D}_{pq}^\xi(\lambda^0)$ are added to the corresponding submatrices of $\hat{\mathcal{D}}_{pq}^\xi(\lambda^0)$, and the first term in Eq. (51) is dropped (cf. Eqs. (30) and (26) in Ref. 31).

The density $\mathcal{D}^f$ for properties of singlet excited states (cf. Eq. (42)) accordingly is

$$\mathcal{D}^f_{pq} = \mathcal{D}^\xi_{pq}(\lambda^f) + \mathcal{D}^\eta_{pq}, \quad \hat{\mathcal{D}}^f_{pq} = \hat{\mathcal{D}}^\xi_{pq}(\lambda^f) + \hat{\mathcal{D}}^\eta_{pq},$$

$$\text{with}\quad \mathcal{D}^\eta_{ij} = -2S_{rr'}\tilde{L}^{ik}_{r's'}S_{s's}R^{jk}_{rs},$$

$$\mathcal{D}^\eta_{rs} = 2\tilde{L}^{ij}_{st}S_{tt'}R^{ij}_{rt'},$$

$$\mathcal{D}^\eta_{ir} = \mathcal{D}^\eta_{ri} = 0,$$

$$\hat{\mathcal{D}}^\eta_{ij} = -\tilde{L}^i_{r'}S_{r'r}R^j_r, \tag{53}$$

$$\hat{\mathcal{D}}^\eta_{rs} = \tilde{L}^i_s R^i_r,$$

$$\hat{\mathcal{D}}^\eta_{ir} = 0,$$

$$\hat{\mathcal{D}}^\eta_{ri} = \tilde{L}^j_{s'}S_{s's}\tilde{R}^{ji}_{sr},$$

and $\tilde{R}^{ij}_{rs} = 2R^{ij}_{rs} - R^{ji}_{rs}$. $\mathcal{D}^\xi(\lambda^f)$ and $\hat{\mathcal{D}}^\xi(\lambda^f)$ are defined according to Eq. (52). $\mathcal{D}^f_{AO}$ again is obtained via Eq. (51). The sum of the $\mathcal{D}^\eta$ and the $\hat{\mathcal{D}}^\eta$ matrix is not identical to the corresponding density matrix for the orbital-unrelaxed case (cf. Eqs. (35) and (27) in Ref. 31). In particular, there are no terms involving the ground state doubles amplitudes in the $\hat{\mathcal{D}}^\eta_{ri}$ block in the orbital-relaxed case, due to the absence of the second term in the $A_{\mu_2\nu_1}$ block of the CC2 Jacobian as specified in Eq. (7) of Ref. 31, which, in turn, is again caused by the presence of the bare rather than the similarity transformed $\mathbf{V_0}$ operator in the Ω_{μ_2} equation (*vide supra*).

For properties of triplet excited states the density matrices $\mathcal{D}^f$, $\hat{\mathcal{D}}^f$, $\mathcal{D}^\xi(\lambda^f)$, and $\hat{\mathcal{D}}^\xi(\lambda^f)$ are identically defined as for the singlet states, but $\mathcal{D}^\eta$ and $\hat{\mathcal{D}}^\eta$ are different, i.e.,

$$\mathcal{D}^\eta_{ij} = -S_{rr'}S_{ss'}\big(\overset{(+)}{\tilde{L}}{}^{ik}_{r's'}\overset{(+)}{R}{}^{jk}_{rs} + 2\overset{(-)}{\tilde{L}}{}^{ik}_{r's'}\overset{(-)}{R}{}^{jk}_{rs}\big),$$

$$\mathcal{D}^\eta_{rs} = S_{tt'}\big(\overset{(+)}{\tilde{L}}{}^{ij}_{st'}\overset{(+)}{R}{}^{ij}_{rt} + 2\overset{(-)}{\tilde{L}}{}^{ij}_{st'}\overset{(-)}{R}{}^{ij}_{rt}\big),$$

$$\mathcal{D}^\eta_{ir} = \mathcal{D}^\eta_{ri} = 0,$$

$$\hat{\mathcal{D}}^\eta_{ij} = -\tilde{L}^i_{r'}S_{r'r}R^j_r, \tag{54}$$

$$\hat{\mathcal{D}}^\eta_{rs} = \tilde{L}^i_s R^i_r,$$

$$\hat{\mathcal{D}}^\eta_{ir} = 0,$$

$$\hat{\mathcal{D}}^\eta_{ri} = \tilde{L}^j_{s'}S_{ss'}\bar{R}^{ji}_{sr},$$

with $\bar{R}^{ij}_{rs} = 2(\overset{(+)}{R}{}^{ij}_{rs} + \overset{(-)}{R}{}^{ij}_{rs})$. $\mathcal{D}^f_{AO}$ again is obtained via Eq. (51). As for singlet excited states the sum of the $\mathcal{D}^\eta$ and the $\hat{\mathcal{D}}^\eta$ matrix is not identical to the corresponding density matrix for the orbital-unrelaxed case, Eq. (43) in Ref. 34; the terms involving the ground state doubles amplitudes in the $\hat{\mathcal{D}}^\eta_{ri}$ block are absent, as above.

III. TEST CALCULATIONS

Orbital-relaxed first order properties for ground and excited states have been implemented in the MOLPRO program package.[44] Most of the relevant routines are parallelized based on a shared file approach. As already discussed earlier, a shared file approach can cause a bottleneck beyond 8–16 cores, depending on the efficiency of the input/output (I/O) subsystem.[34] The correctness of the code was verified by comparing the results of our program using untruncated pair lists and full domains to the corresponding canonical results obtained with the TURBOMOLE program,[25,27,28,45] and to numerical results obtained from finite differences.

The accuracy of the local approximations introduced by restricted pair lists and domains is analysed by comparing local and canonical results for the same test set of molecules and excited states as used previously.[32–34] The cc-pVDZ and aug-cc-pVDZ AO basis sets[46] are employed together with the related fitting basis sets optimized for DF-MP2.[47] In calculations employing the aug-cc-pVDZ basis, the contributions of the most diffuse functions of each angular momentum are discarded in the Pipek-Mezey localization procedure (cpldel=1 option in MOLPRO).[42] This is generally advisable to achieve better localization of the LMOs for basis sets with diffuse functions.

In all calculations presented here, three Laplace quadrature points (LP) were used. For orbital-unrelaxed properties it was already demonstrated in earlier publications that three LPs provide sufficient accuracy.[32,34] In the course of this work this was also verified for orbital-relaxed properties by comparing for some test molecules and states calculations performed with three and five LPs. It turned out that for both basis sets the effect of this increase in the number of LPs is typically between one and two orders of magnitude smaller than the error introduced by the local approximation, very similar as for orbital-unrelaxed properties.

A. Approximate Lagrangians for LT-DF-LCC2

As discussed in detail in Ref. 48 for the LT-LMP2 method the Lagrangians in Eqs. (24) and (37) are not the proper energy Lagrangians, if the Laplace transformation is employed, but just approximations to it, while the proper LT-DF-LCC2 Lagrangians are impractical (cf. Eq. (27) in Ref. 48 and the related discussion). Yet the errors introduced by the use of these approximate Lagrangians without further conditions turned out to be small for the LT-LMP2 method and the properties were even slightly closer to the canonical reference than the ones calculated with the standard LMP2 method.

Here, we explore the effect of these approximate Lagrangians on the CC2 orbital-relaxed ground state dipole moments. For the ground state properties the Laplace transform is used to partition the $\tilde{\lambda}^0$ equation system as discussed in Sec. II A, Eqs. (15)–(21). Table I lists the z-component of the CC2 ground state dipole moment, calculated in the cc-pVDZ basis using standard domains (iext=0) and extended domains (iext=1, cf. Sec. III B), for several molecules. Results for the analytical canonical and local methods without (DF-LCC2[30,31]) and with Laplace transform (LT-DF-LCC2) are compared, and also the corresponding numerical results from finite difference calculations are included. As can be seen, analytical and numerical results differ slightly (by up to 0.002 a.u.) for LT-DF-LCC2, while they are identical for DF-LCC2. A similar effect is observed also for excited states. One can therefore

TABLE I. The z-component (in a.u.) of the orbital-relaxed ground state dipole moment vector is shown for several molecules. Analytical canonical results are shown together with analytical and numerical local results obtained with the DF-LCC2 and the LT-DF-LCC2 method.

| | Can. | iext=0 | | | | iext=1 | | | |
| | | DF-LCC2 | | LT-DF-LCC2 | | DF-LCC2 | | LT-DF-LCC2 | |
	An.	An.	Num.	An.	Num.	An.	Num.	An.	Num.
DMABN	2.895	2.875	2.875	2.875	2.875	2.891	2.891	2.890	2.891
HPA	0.345	0.360	0.360	0.358	0.360	0.347	0.347	0.347	0.347
Propanamide	−1.305	−1.311	−1.311	−1.310	−1.311	−1.305	−1.305	−1.305	−1.305
trans-urocanic acid	1.923	1.934	1.934	1.934	1.934	1.921	1.921	1.922	1.921

conclude that the use of the approximate Lagrangians, Eqs. (24) and (37), for LT-DF-LCC2 is uncritical for the calculation of first-order properties.

For geometry optimizations the effect of the approximate Lagrangians is expected to be larger. At the moment an optimization routine based on the presented work is developed, which combines the advantages of DF-LCC2 and LT-DF-LCC2.

B. Pair approximations and domains

For the ground state the truncation of the LMO pair lists depends solely on the respective LMO interorbital distance R_g. For excited states, on the other hand, adaptive pair lists are employed, as explained in detail in Sec. II C of Ref. 32: a set of important LMOs is determined for each individual state (specified by threshold $\kappa_e = 0.999$) and state-specific pair lists are determined from the list of these important orbitals. Such a pair list, corresponding to a certain excited state, comprises all pairs of important LMOs related to that state, and all other pairs up to a certain LMO interorbital distance R_{ex}. Moreover, all pairs from the ground state list are also included.

In order to find reliable values for R_g and R_{ex}, various calculations with different pair truncations were performed employing the cc-pVDZ basis set for some molecules from the test set. Table II compiles the norm of the ground state canonical dipole moment vector, and for the two lowest singlet and triplet excited states the norm of the canonical dipole moment difference vector (excited state minus ground state dipole moment), all without and with orbital relaxation. Furthermore, the relative error of the corresponding local calculation is given as the ratio of the norm of the difference vector (canonical minus local), and the norm of the canonical vector. The ratios of the lengths of truncated and full pair lists are also given in Table II.

In previous work devoted to orbital-unrelaxed first-order properties pair list specifications of $R_g/R_{ex} = 10/5$ bohr were usually employed. In Table II, we compare orbital-unrelaxed and relaxed results for pair lists determined by $R_g/R_{ex} = 10/5$, 5/3, and 15/10 bohr.

R_g affects the excited state properties through the ground state amplitudes t_{μ_2} and multipliers $\tilde{\lambda}^0_{\mu_2}$, which are restricted to the ground state pair lists and domains. The left and right eigenvectors $\tilde{L}_{\mu_2}$ and R_{μ_2} are restricted to the excited state

TABLE II. Norms (in a.u.) of the canonical ground state dipole vector $|\mu^0|$ and the canonical dipole difference vectors of the excited states $|\mu^f|$ without orbital relaxation are shown in column $|\mu^{can}|$. The corresponding orbital-relaxed quantities are labeled by the index *rel*. The results for the local calculations with the pair lists criterion combinations 5/3, 10/5, and 15/10 are given as the ratio of the norm of the difference vector (canonical minus local) relative to the canonical value $|\delta\mu|/|\mu^{can}|$ in %. The last three columns contain the percentage of included pairs.

| | State | $|\mu^{can}|$ | $|\delta\mu|/|\mu^{can}|$ | | | $|\mu^{can}_{rel}|$ | $|\delta\mu_{rel}|/|\mu^{can}_{rel}|$ | | | Included pairs | | |
			5/3	10/5	15/10		5/3	10/5	15/10	5/3	10/5	15/10
β-Dipeptide	S_0	0.423	3.1	0.6	0.5	0.415	2.3	0.3	0.3	57	85	98
	S_1	0.388	23.9	23.7	23.5	0.262	30.3	29.9	29.9	76	87	100
	S_2	0.760	3.1	3.6	3.9	0.607	3.5	3.2	3.1	71	85	98
	T_1	0.436	12.1	11.8	11.6	0.328	13.3	13.0	13.0	78	92	100
	T_2	0.366	9.3	9.1	8.2	0.355	8.4	7.8	7.4	74	86	99
HPA	S_0	0.734	3.2	1.1	0.6	0.756	2.7	0.7	0.4	57	82	98
	S_1	0.242	3.9	1.9	2.5	0.203	1.4	2.7	3.6	77	87	100
	S_2	0.624	7.8	6.2	5.4	0.507	8.3	6.0	5.4	77	86	99
	T_1	0.109	13.4	4.2	5.0	0.091	9.3	3.6	4.9	77	91	100
	T_2	0.332	5.3	1.7	1.3	0.293	2.9	1.2	0.6	74	86	100
trans-urocanic acid	S_0	1.904	0.6	0.2	0.1	1.935	0.8	0.1	<0.1	66	92	100
	S_1	2.310	2.0	0.4	0.4	1.990	1.4	0.8	0.8	92	100	100
	S_2	2.261	0.7	1.4	1.6	2.104	2.2	2.0	2.0	100	100	100
	T_1	0.385	0.9	0.6	0.4	0.340	6.6	0.7	0.3	99	100	100
	T_2	0.312	18.6	3.1	2.1	0.326	12.9	1.5	0.6	90	97	100

TABLE III. Norms (in a.u.) of the canonical ground state dipole vector $|\mu^0|$ and the canonical dipole difference vectors of the excited states $|\mu^f|$ without orbital relaxation are shown in column $|\mu^{can}|$. The corresponding orbital-relaxed quantities are labeled by the index *rel*. The results for the local calculations using the default domains (iext=0) and the domains, which are extended by the nearest neighbours (iext=1), are given as the ratio of the norm of the difference vector (canonical minus local) relative to the canonical value $|\delta\mu|/|\mu^{can}|$ in %. The last two columns contain the ratio (local vs. canonical) of the number of unique elements of the doubles quantities for the calculations in %.

| | State | $|\mu^{can}|$ | $|\delta\mu|/|\mu^{can}|$ | | $|\mu_{rel}^{can}|$ | $|\delta\mu_{rel}|/|\mu_{rel}^{can}|$ | | Doubles ratio | |
			iext=0	iext=1		iext=0	iext=1	iext=0	iext=1
β-Dipeptide	S_0	0.423	3.8	0.6	0.415	2.6	0.3	7	31
	S_1	0.388	26.7	23.7	0.262	34.0	29.9	22	41
	S_2	0.760	5.3	3.6	0.607	5.7	3.2	11	36
	T_1	0.436	13.4	11.8	0.328	14.9	13.0	25	47
	T_2	0.366	26.6	9.1	0.355	23.2	7.8	17	39
HPA	S_0	0.734	5.8	1.1	0.756	2.8	0.7	7	32
	S_1	0.242	2.5	1.9	0.203	3.1	2.7	25	46
	S_2	0.624	8.1	6.2	0.507	7.6	6.0	21	44
	T_1	0.109	13.9	4.2	0.091	10.3	3.6	23	47
	T_2	0.332	4.2	1.7	0.293	2.0	1.2	23	44
trans-urocanic	S_0	1.904	1.6	0.2	1.935	0.6	0.1	15	55
acid	S_1	2.310	2.7	0.4	1.990	2.3	0.8	32	70
	S_2	2.261	1.1	1.4	2.104	2.1	2.0	50	76
	T_1	0.385	6.0	0.6	0.340	0.8	0.7	41	71
	T_2	0.312	21.7	3.1	0.326	12.2	1.5	52	75

pair lists and domains, which also contain the ground state pair lists and domains.

As is evident from Table II, the errors clearly become smaller when going from 5/3 to longer pair lists. Yet already 10/5 provides sufficiently accurate results, whereas 15/10 shows no substantial further improvement, but already produces very long pair lists. Note that the results for state S_2 of *trans*-urocanic acid with different R_g/R_{ex} differ due to different ground-state pair lists, while the excited state pair list is full in all three cases.

Overall, the effect of pair list truncation is very similar for the orbital-relaxed and unrelaxed case, and the default settings already used previously of $R_g/R_{ex} = 10/5$ bohr appears to be a good choice, which will be employed in all further calculations of the present work.

The domains for the ground state truncating the pair-specific virtual space are built by using the Boughton Pulay (BP) procedure with a criterion of 0.98.[49] The excited state domains are obtained in an adaptive procedure as explained in detail in Sec. II C of Ref. 32. The orbital domains are determined by specifying an ordered list of important centers for each important LMO. The ground state domains then are augmented with further centers from this list until a threshold of 0.98 is reached by the least-squares optimization procedure introduced in Sec. II C of Ref. 32.

As discussed earlier, such domains are appropriate for the calculation of excitation energies, but for orbital-unrelaxed properties it was observed that augmenting these domains by further centers leads to significantly improved accuracy. Such extended domains can be constructed by, e.g., adding further centers to the BP ground state domain, which are separated by not more than one bond from the closest atom in the original BP domain (iext=1 option in MOLPRO).

In order to investigate this aspect also for orbital-relaxed properties, calculations with default (iext=0) and

augmented (iext=1) domains were performed for some molecules of the test set in the cc-pVDZ basis. Table III compiles the norm of the canonical dipole moment vector for the ground state, and the canonical dipole moment difference vector μ^f (excited state minus ground state dipole moment) for the two lowest lying singlet and triplet excited states of these molecules, along with the relative errors of the local method employing iext=0 and iext=1, respectively. Furthermore, the ratios local/canonical of the number of unique elements of the doubles vector of the ground state amplitudes, and excited state eigenvectors, respectively, are shown.

Again the behavior of orbital-unrelaxed and relaxed properties is very similar. For some of the states the iext=0 and iext=1 results are very similar, but there are some cases like the T_2 state of the *trans*-urocanic acid molecule, where the domain extension leads to a drastic improvement of the accuracy. It is therefore recommended to use extended domains also in calculations of orbital-relaxed properties. For all remaining calculations presented in this contribution the iext=1 option was employed.

C. Accuracy of the local approximations

As already mentioned above, the accuracy of the local approximations was checked by comparing local and canonical calculations for a set of test molecules and excited singlet and triplet states already used in previous work.[32–34] The orbital-unrelaxed dipole moments differ from the ones published in Refs. 33 and 34 because of a lower convergence threshold for the ground state (default convergence threshold for gradients), which was employed in the present calculations.

Table IV compiles the norms of the orbital-unrelaxed and relaxed canonical reference dipole moments for the ground state and the two lowest singlet and triplet states of these molecules, along with deviations of the local

TABLE IV. Column $|\mu^{can}|$ shows the norms (in a.u.) of the orbital-unrelaxed canonical ground state dipole vector $|\mu^0|$ and for the individual excited states the corresponding difference vectors $|\mu^f|$ (with respect to $|\mu^0|$). Similarly, column $|\mu^{can}_{rel}|$ contains the related orbital-relaxed values. The results of the local calculations are given as the ratio of the norm of the difference vector (canonical minus local) relative to the canonical norm, $|\delta\mu|/|\mu^{can}|$ in %. For each excited state also the canonical excitation energy ω_{can} and the character of the excitation is listed.

| | | cc-pVDZ | | | | | | aug-cc-pVDZ | | | | |
| | | | | Orbital-unrelaxed | | Orbital-relaxed | | | | Orbital-unrelaxed | | Orbital-relaxed | |
	State	ω_{can}	Char.	$|\mu^{can}|$	$|\delta\mu|/|\mu^{can}|$	$|\mu^{can}_{rel}|$	$|\delta\mu_{rel}|/|\mu^{can}_{rel}|$	ω_{can}	Char.	$|\mu^{can}|$	$|\delta\mu|/|\mu^{can}|$	$|\mu^{can}_{rel}|$	$|\delta\mu_{rel}|/|\mu^{can}_{rel}|$
β-Dipeptide	S_0			0.423	0.6	0.415	0.3			0.436	0.6	0.427	1.2
	S_1	4.861	$n \to \pi^*$	0.388	23.7	0.262	29.9	4.715	$n \to \pi^*$	0.372	23.4	0.249	34.2
	S_2	5.825	$n \to \pi^*$	0.760	3.6	0.607	3.2	4.982	$n \to Ry$	1.557	22.9	1.336	25.7
	T_1	4.496	$n \to \pi^*$	0.436	11.8	0.328	13.0	4.418	$n \to \pi^*$	0.444	11.6	0.326	15.6
	T_2	5.387	$\pi \to \pi^*$	0.366	9.1	0.355	7.8	4.935	$n \to Ry$	1.475	18.7	1.289	20.5
Dipeptide	S_0			1.304	0.1	1.330	0.2			1.339	0.2	1.365	0.1
	S_1	5.871	$n \to \pi^*$	0.735	2.8	0.587	1.6	5.743	$n \to \pi^*$	0.963	7.6	0.799	9.3
	S_2	6.106	$n \to \pi^*$	0.740	4.2	0.602	3.0	5.864	$n \to Ry$	0.984	4.9	0.749	6.3
	T_1	5.504	$n \to \pi^*$	0.789	2.3	0.668	1.0	5.440	$n \to \pi^*$	0.963	3.7	0.830	4.3
	T_2	5.763	$n \to \pi^*$	0.794	2.2	0.681	1.4	5.669	$n \to \pi^*$	0.954	3.6	0.829	3.9
DMABN	S_0			2.904	<0.1	2.895	0.2			3.039	<0.1	3.042	0.1
	S_1	4.525	$\pi \to \pi^*$	0.935	1.2	0.793	1.3	4.323	$\pi \to \pi^*$	1.003	0.5	0.844	0.8
	S_2	4.891	$\pi \to \pi^*$	2.072	0.3	1.793	0.5	4.495	$\pi \to Ry$	2.806	1.9	2.838	1.8
	T_1	3.716	$\pi \to \pi^*$	0.807	0.2	0.710	0.8	3.648	$\pi \to \pi^*$	0.892	0.4	0.789	0.7
	T_2	4.184	$\pi \to \pi^*$	1.181	1.1	1.058	1.0	4.011	$\pi \to \pi^*$	1.213	0.3	1.078	0.4
Guanine	S_0			2.512	0.1	2.563	0.1			2.542	0.1	2.601	0.1
	S_1	5.316	$\pi \to \pi^*$	0.340	3.2	0.258	1.9	4.743	$\pi \to Ry$	4.374	10.4	4.210	10.4
	S_2	5.660	$n \to \pi^*$	1.390	1.7	1.090	1.4	5.022	$\pi \to \pi^*$	0.628	0.7	0.541	2.4
	T_1	4.506	$\pi \to \pi^*$	0.658	1.2	0.595	0.1	4.310	$\pi \to \pi^*$	0.515	12.2	0.448	12.9
	T_2	4.566	$\pi \to \pi^*$	0.372	2.3	0.341	3.0	4.400	$\pi \to \pi^*$	0.274	3.9	0.241	2.3
HPA	S_0			0.734	1.1	0.756	0.7			0.726	0.6	0.748	0.9
	S_1	4.984	$\pi \to \pi^*$	0.242	1.9	0.203	2.7	4.816	$\pi \to \pi^*$	0.203	4.0	0.160	4.9
	S_2	6.149	$n \to \pi^*$	0.624	6.2	0.507	6.0	5.216	$\pi \to Ry$	4.510	3.5	4.460	3.6
	T_1	4.254	$\pi \to \pi^*$	0.109	4.2	0.091	3.6	4.189	$\pi \to \pi^*$	0.106	1.7	0.086	2.1
	T_2	4.582	$\pi \to \pi^*$	0.332	1.7	0.293	1.2	4.433	$\pi \to \pi^*$	0.285	1.8	0.246	1.6
p-cresol	S_0			0.521	1.1	0.528	0.8			0.519	0.4	0.533	0.3
	S_1	4.982	$\pi \to \pi^*$	0.256	1.8	0.218	3.8	4.795	$\pi \to \pi^*$	0.253	1.7	0.210	2.4
	S_2	6.326	$\pi \to \pi^*$	0.832	1.1	0.741	1.4	5.145	$\pi \to Ry$	4.280	4.6	4.209	4.6
	T_1	4.228	$\pi \to \pi^*$	0.165	3.4	0.146	1.9	4.156	$\pi \to \pi^*$	0.194	2.9	0.173	2.5
	T_2	4.588	$\pi \to \pi^*$	0.305	1.9	0.269	0.8	4.421	$\pi \to \pi^*$	0.273	1.6	0.239	1.2
N-acetylglycine	S_0			1.070	0.1	1.085	0.1			1.035	0.2	1.050	0.2
	S_1	5.862	$n \to \pi^*$	0.741	3.4	0.591	2.0	5.732	$n \to \pi^*$	0.948	6.9	0.784	8.1
	S_2	6.252	$n \to \pi^*$	0.594	1.2	0.477	1.3	5.989	$n \to Ry$	2.218	12.6	1.974	13.9
	T_1	5.489	$n \to \pi^*$	0.793	2.7	0.671	1.2	5.421	$n \to \pi^*$	0.962	3.9	0.828	4.4
	T_2	5.883	$n \to \pi^*$	0.659	1.2	0.563	1.0	5.779	$n \to \pi^*$	0.667	1.6	0.567	1.8
Phenylalanine	S_0			1.755	0.3	1.790	0.1			1.787	0.1	1.831	0.2
	S_1	5.260	$\pi \to \pi^*$	0.015	36.7	0.013	30.8	5.152	$\pi \to \pi^*$	0.053	11.2	0.050	8.2
	S_2	5.827	$n \to Ry$	0.571	12.6	0.459	13.0	5.693	$n \to Ry$	0.623	6.1	0.503	6.4
	T_1	4.304	$\pi \to \pi^*$	0.016	19.7	0.017	9.8	4.273	$\pi \to \pi^*$	0.021	8.5	0.020	11.9
	T_2	5.089	$\pi \to \pi^*$	0.027	14.4	0.025	7.7	4.976	$\pi \to \pi^*$	0.068	3.9	0.065	4.1
1-phenylpyrrole	S_0			0.697	0.1	0.688	0.1			0.689	0.3	0.683	0.3
	S_1	5.073	$\pi \to \pi^*$	0.883	0.6	0.803	0.3	4.921	$\pi \to \pi^*$	1.100	0.5	1.002	0.5
	S_2	5.555	$\pi \to \pi^*$	2.381	0.1	2.186	0.2	5.309	$\pi \to \pi^*$	2.236	0.5	2.061	0.4
	T_1	4.181	$\pi \to \pi^*$	0.343	0.4	0.313	0.2	4.127	$\pi \to \pi^*$	0.416	0.9	0.378	0.2
	T_2	4.492	$\pi \to \pi^*$	1.490	2.1	1.426	1.7	4.391	$\pi \to \pi^*$	1.479	5.6	1.408	4.3
Propanamide	S_0			1.312	0.2	1.358	<0.1			1.373	<0.1	1.423	0.2
	S_1	5.926	$n \to \pi^*$	0.789	5.1	0.641	5.1	5.667	$n \to \pi^*$	1.026	9.4	0.861	10.9
	S_2	7.491	$n \to Ry$	2.646	1.7	2.336	1.7	5.755	$n \to Ry$	3.713	2.2	3.439	2.3
	T_1	5.555	$n \to \pi^*$	0.836	4.0	0.716	3.6	5.368	$n \to \pi^*$	1.033	5.9	0.901	6.5
	T_2	6.134	$\pi \to \pi^*$	0.794	2.4	0.756	1.9	5.719	$n \to Ry$	3.550	7.2	3.283	7.6
Tyrosine	S_0			1.320	0.4	1.357	0.3			1.409	0.5	1.456	0.3
	S_1	4.995	$\pi \to \pi^*$	0.222	2.6	0.183	2.0	4.834	$\pi \to \pi^*$	0.192	2.8	0.151	3.1
	S_2	5.824	$n \to Ry$	0.570	11.8	0.456	12.2	5.292	$\pi \to Ry$	4.157	13.6	4.118	13.4
	T_1	4.243	$\pi \to \pi^*$	0.101	9.7	0.080	7.0	4.176	$\pi \to \pi^*$	0.130	2.0	0.108	2.2
	T_2	4.621	$\pi \to \pi^*$	0.352	2.5	0.312	1.3	4.481	$\pi \to \pi^*$	0.304	1.1	0.267	1.1

TABLE IV. (*Continued.*)

				cc-pVDZ						aug-cc-pVDZ			
				Orbital-unrelaxed		Orbital-relaxed				Orbital-unrelaxed		Orbital-relaxed	
	State	ω_{can}	Char.	$|\mu^{can}|$	$|\delta\mu|/|\mu^{can}|$	$|\mu^{can}_{rel}|$	$|\delta\mu_{rel}|/|\mu^{can}_{rel}|$	ω_{can}	Char.	$|\mu^{can}|$	$|\delta\mu|/|\mu^{can}|$	$|\mu^{can}_{rel}|$	$|\delta\mu_{rel}|/|\mu^{can}_{rel}|$
trans-urocanic	S_0			1.904	0.2	1.935	0.1			2.030	0.3	2.077	0.1
acid	S_1	4.987	$n \to \pi^*$	2.310	0.4	1.990	0.8	4.863	$n \to \pi^*$	2.285	1.0	1.949	0.9
	S_2	5.207	$\pi \to \pi^*$	2.261	1.4	2.104	2.0	4.931	$\pi \to \pi^*$	2.202	2.3	2.061	2.7
	T_1	3.377	$\pi \to \pi^*$	0.385	0.6	0.340	0.7	3.308	$\pi \to \pi^*$	0.466	0.9	0.416	0.2
	T_2	5.050	$\pi \to \pi^*$	0.312	3.1	0.326	1.5	4.671	$n \to \pi^*$	2.232	1.1	1.955	0.8

calculations from the canonical values. These deviations are again calculated as the ratio of the norm of the difference vector between local and canonical dipole moment, and the norm of the canonical dipole moment, respectively.

As already discussed earlier by Köhn and Hättig, the difference between orbital-relaxed and unrelaxed canonical dipole moments is for excited states generally larger than for the ground state.[28] For the ground state a large part of the orbital relaxation is already provided by the $\mathbf{T_1}$ operators and the orbital relaxation effects in the test set are in the range of 1%–3%. Yet for excited states the orbital relaxation effects can become clearly larger than for the ground state; e.g., for the S_1 state of Dipeptide in the cc-pVDZ basis the norm of the unrelaxed dipole moment amounts to $|\mu| = 0.735$ a.u., which decreases to $|\mu_{rel}| = 0.587$ a.u. when orbital relaxation effects are taken into account.

The relative deviation of the local ground state dipole moments from the canonical reference is for both basis sets in most cases smaller than 1%. For singlet and triplet excited states the relative deviations are substantially larger, but usually clearly below 10%. For phenylalanine the deviations are larger, because the absolute values are tiny.

For the S_1 ($n \to \pi^*$) state of the β-Dipeptide a particularly large deviation between the local and the canonical calculation was observed (more than 20% for the cc-pVDZ basis; for the aug-cc-pVDZ basis even more). On the other hand, the structurally very similar Dipeptide did not exhibit such deviations. Plots of the density difference between excited and

ground states, as shown in Fig. 1, do not reveal any significant discrepancies between the canonical and the local case. For comparison, the density difference of the S_2 ($n \to \pi^*$) state, for which canonical and local dipole moment vectors are in much better agreement, is also shown. Extending the pair lists or increasing the number of Laplace quadrature points in the β-Dipeptide calculation does not improve the results. On the other hand, the canonical result is retrieved to good accuracy with an increased domain threshold. By augmenting the domains stepwise by individual atoms the discrepancy between the canonical and the local calculation can finally be traced to two H-atoms of the C-atom in α position to the carbonyl group, where the excitation to the S_1 state is located. With default threshold, these two H-atoms, which are in `cis`-position to the O-atom of the carbonyl group, are not included in the respective domain related to the LMOs of the carbonyl group. Including these two atoms reduces the deviation from the canonical result for the dipole moment difference vector to 5.0%, and to 6.8% with, and without orbital relaxation. Note that neither for the S_2 state of β-Dipeptide nor for the S_1 and S_2 states of Dipeptide such H-atoms in `cis`-position to the O-atom of the carbonyl group relevant for the particular excitations do occur. Furthermore, omitting these H-atoms in the relevant domains of the S_1 state calculation, but employing a bigger basis set on the C and O atoms of the carbonyl group also leads to a deviation of less than 10% between the local and the respective canonical result. Based on these observations, basis set superposition error (BSSE) effects in the
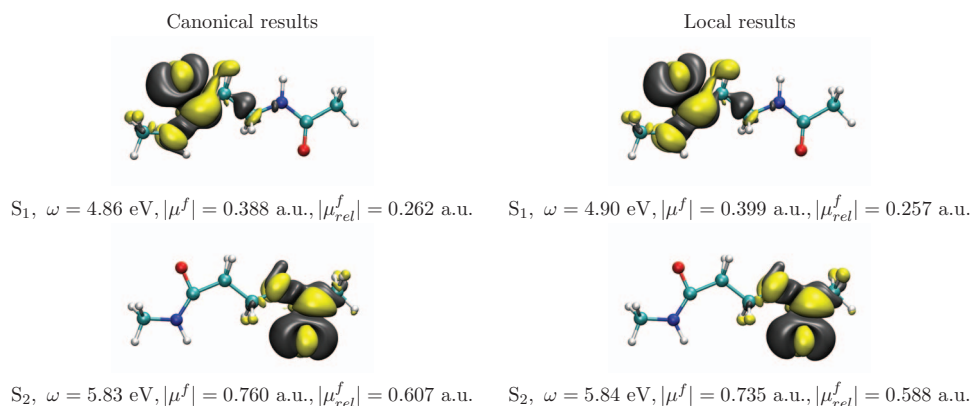
Canonical results   Local results

S_1, $\omega = 4.86$ eV, $|\mu^f| = 0.388$ a.u., $|\mu^f_{rel}| = 0.262$ a.u. S_1, $\omega = 4.90$ eV, $|\mu^f| = 0.399$ a.u., $|\mu^f_{rel}| = 0.257$ a.u.

S_2, $\omega = 5.83$ eV, $|\mu^f| = 0.760$ a.u., $|\mu^f_{rel}| = 0.607$ a.u. S_2, $\omega = 5.84$ eV, $|\mu^f| = 0.735$ a.u., $|\mu^f_{rel}| = 0.588$ a.u.

FIG. 1. Canonical and local orbital-relaxed density differences between the two lowest singlet excited states and the ground state of the β-Dipeptide molecule (cc-pVDZ basis set). The yellow (bright) and dark grey iso-surfaces represent a value of $+0.002$ and -0.002, respectively.

$S_1, \omega = 2.7$ eV, $|\mu^f| = 7.15$ a.u., $|\mu^f_{rel}| = 7.06$ a.u. $T_1, \omega = 2.0$ eV, $|\mu^f| = 1.64$ a.u., $|\mu^f_{rel}| = 1.63$ a.u.
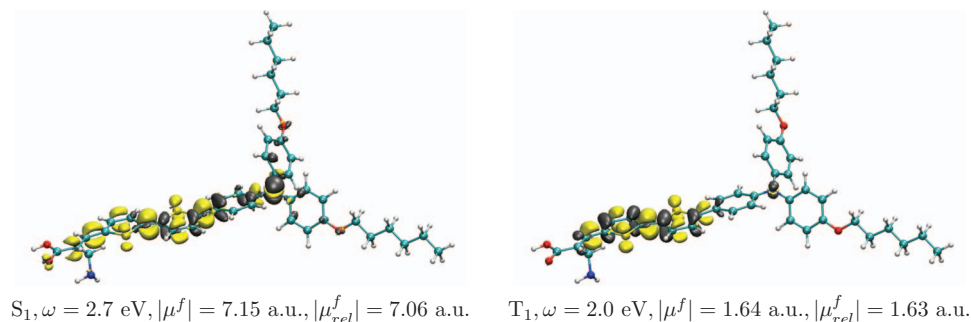
FIG. 2. Orbital-relaxed density differences between the lowest singlet and triplet excited states and the ground state of the D21L6 molecule. The yellow (bright) and dark grey iso-surfaces represent a value of $+0.002$ and -0.002, respectively. The orbital unrelaxed density differences are not shown explicitly, because they look very similar (cf. Fig. 2 in Ref. 34).

canonical calculation may be a possible explanation for the discrepancy between the local and the canonical result. The local method might provide a more balanced description of, e.g., the dipoles of the S_1 state *vs.* that of the S_2 state.

For the majority of the excited states calculated in the cc-pVDZ basis, the deviations of the local from the canonical results are smaller when orbital relaxation is taken into account. In the aug-cc-pVDZ basis, on the other hand, the deviations appear to be slightly larger for the orbital-relaxed results.

D. Efficiency of the code

As an illustrative example for the efficiency of the new code we present results from calculations on the D21L6 (3-(5-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophene-2-yl)thiophene-2-yl)-2-cyanoacrylic acid) molecule, an organic sensitizer for solar-cell applications.[50] The D21L6 molecule was already used by us as an example in earlier work[34,44] and comprises 98 atoms, 262 correlated electrons, and 948 basis functions in the cc-pVDZ AO basis. The norms of the orbital-unrelaxed and relaxed dipole moments of the ground state and the four lowest singlet and triplet excited states are given in Table V. For the D21L6 molecule substantial savings are achieved by the local method: the ratios of the lengths of truncated *vs.* full pair lists are about 30% for the ground state, and between 48% and 64% for the calculated excited states. The ratio local *vs.* canonical of the number of unique elements of the doubles vector is less than 1% for the ground state amplitudes, and between less than 6% (state T_1) and about 19% (state S_3 and S_4) for the excited state eigenvectors. The maximum ratio is quite large, because the domains of the states S_3 and S_4 are unified during the Davidson iterations, for all other states they lie below 10%.

The experimentally observed absorption maximum in the visible region at 2.71 eV with a high molar extinction coefficient, which was assigned to a $\pi \rightarrow \pi^*$ CT transition,[50] corresponds to the $S_0 \rightarrow S_1$ transition in Table V. The calculated excitation energy of the S_1 state of 2.79 eV (2.74 eV in Ref. 44 due to a different convergence threshold, cf. Sec. III C) is in excellent agreement with the experimental value, probably due to fortuitous can-

cellation of errors given the relatively modest AO basis that has been used. Also the calculated transition strength of 1.35 a.u. is sizable and thus is compatible with a high extinction coefficient, as observed in the experiment. The CT character of the S_1 state is indicated by the large increase in the dipole moment along the direction of the residue carrying the thiophene groups, on going from the S_0 to the S_1 state (cf. Table V and Fig. 2). The S_2 state also has some CT character, whereas the two lowest triplet states show no charge transfer,[34] as is also indicated by the much smaller dipole moment changes in Table V.

The calculation was run in parallel on seven AMD Opteron 6180 SE @ 2.50 GHz cores. The common shared file system was striped over four SAS disks. The timings for finding the left and right eigenvectors of the Jacobian and for the calculation of orbital unrelaxed properties were discussed in detail in earlier publications,[32,34] here the emphasis is on the additional time needed for the orbital relaxation. The detailed timings for the most time-consuming steps are listed in Table V. Altogether for each excited state the calculation of orbital-relaxed properties (without calculation of the left eigenvector) takes about 10–11 h, 40% of this time is needed for the parts, which also have to be calculated for unrelaxed properties, the rest is needed for the additional routines for orbital relaxation. The largest fraction of the CPU and elapsed time is required for the calculation of the intermediates for the linear *z-vector equations*, i.e., $B_{\mu i}$, $B_{\mu r}$, $B_{r\mu}$ (Eqs. (A5)–(A7) for the ground state, Eqs. (B3)–(B5) for singlet excited states, and Eqs. (C4)–(C6) for triplet excited states). For the ground state this step takes about 1.5 h, while for the excited states about 5–6 h are needed per state (except for the states S_3 and S_4 with unified domains, where about 8 h are required). Solving the linear *z-vector equations*, on the other hand, takes less than half an hour per state (almost entirely for the Z-CPHF equations, while the Z-CPL equations take virtually no time). About 30% of the time for the intermediates $B_{\mu i}$, $B_{\mu r}$, $B_{r\mu}$ is needed for the terms including $g(d)$ (cf. Eq. (A8)) and about the same fraction for the calculation of $d^{f(LR)}$ (cf. Eqs. (B8) and (C7)). The contractions with half transformed integrals require about 15% of the time. For the states S_3 and S_4 the calculation of $d^{f(LR)}$ is much more time-consuming, thus the time ratios differ.

TABLE V. Results and timings for the few lowest singlet and triplet states of D21L6: Column $|\mu|$ shows the norms (in a.u.) of the orbital-unrelaxed local ground state dipole vector $|\mu^0|$ and for the individual excited states the corresponding difference vectors $|\mu^f|$ (with respect to $|\mu^0|$). Similarly, column $|\mu_{rel}|$ contains the related orbital-relaxed values. For each individual excited state also the local excitation energy ω and the character of the excitation is listed. The timings (in minutes) were obtained on 7 cores, AMD Opteron 6180 SE @ 2.50 GHz.

State	ω	Char.	$|\mu|$	$|\mu_{rel}|$	$t(\tilde{\lambda})$[a]	$t(\mathcal{D}^f)$[b]	$t(d^{f(LR)})$[c]	$t(B)$[d]	$t(HT)$[e]	$t(g)$[f]	$t(z)$[g]
S_0			2.670	2.711	227			113	9	73	31
S_1	2.787	CT	7.151	7.058	275	6	62	309	67	110	31
S_2	3.634	CT	5.142	4.918	269	5	59	302	66	106	32
S_3	3.735[h]	$\pi \to \pi^*$	0.152[h]	0.319[h]	253	13	237	478	63	105	31
S_4	3.933[h]	CT	5.535[h]	5.332[h]	276	13	237	492	72	108	31
T_1	2.041	$\pi \to \pi^*$	1.638	1.625	237	8	81	319	58	111	25
T_2	2.726	$\pi \to \pi^*$	2.307	2.260	235	8	88	322	58	108	30
T_3	3.438[h]	$\pi \to \pi^*$	1.510[h]	1.472[h]	229	9	114	354	58	111	29
T_4	3.554[h]	$\pi \to \pi^*$	0.293[h]	0.313[h]	241	10	135	372	64	106	31

[a]Elapsed time for the calculation of Lagrange multipliers $\tilde{\lambda}$ for this state.
[b]Elapsed time for the calculation of the density $\mathcal{D}^f$ (cf. Eqs. (51)–(54)).
[c]Elapsed time for the calculation of $d^{f(LR)}$ (cf. Eqs. (B8) and (C7)).
[d]Elapsed time for the calculation of $B_{\mu i}, B_{\mu r}, B_{r\mu}$ (cf. Eqs. (A5)–(A7), (B3)–(B5), and (C4)–(C6)).
[e]Elapsed time for the terms of $B_{\mu i}, B_{\mu r}, B_{r\mu}$ including contractions with half transformed integrals.
[f]Elapsed time for the terms of $B_{\mu i}, B_{\mu r}, B_{r\mu}$ including $g(d)$.
[g]Elapsed time for solving the linear *z-vector equations*.
[h]These results have to be taken with a grain of salt, because only a total of four states was calculated.

Using the settings described above, a calculation involving the four lowest singlet and triplet excited states of a system of this size can be performed within about 4 weeks (triplet about 1.5 weeks, singlet about 2.5 weeks mainly due to large unified domains for states S_3 and S_4). The largest amount of the time is needed for solving the left and right eigenvalue equation of the Jacobian, while the Lagrange multipliers and densities for the properties are calculated within about half a day per state.

IV. CONCLUSIONS

In this contribution we report formalism, implementation, and test calculations for orbital-relaxed first-order properties of excited states in the context of the local CC2 response method LT-DF-LCC2. The new method extends the scope for calculations of CC2 excited state properties to extended molecular systems, which were accessible so far only by TD-DFT. The utilization of the Laplace transformation enables multistate calculations and state-specific local approximations. It is demonstrated that the deviations of the local results from canonical reference values are very similar for orbital-relaxed and orbital unrelaxed properties. For our benchmark set of test molecules and excited states these deviations are smaller than 10%, though there are some exceptions.

As an illustrative application example the lowest four singlet and triplet excited states of 3-(5-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophene-2-yl)thiophene-2-yl)-2-cyanoacrylic acid (D21L6), an organic sensitizer for solar-cell applications, were calculated. The lowest excited singlet state corresponds to a CT transition with a large change in the dipole moment and sizable transition strength, in agreement with the experiment, while the lowest triplet states show no CT character. For systems of this size (about hundred atoms), the calculation of excitation energies, orbital-unrelaxed and orbital-relaxed dipole moments of the four lowest singlet and triplet excited states can be performed within about 4 weeks.

The next step is the implementation of analytic gradients with respect to nuclear displacements for excited states in the framework of local CC2 response. Such an implementation is presently under development.

ACKNOWLEDGMENTS

APPENDIX A: WORKING EQUATIONS FOR THE GROUND STATE

The quantity $\mathbf{B^0}$ (cf. Eqs. (30) and (33)) is the derivative of $\mathcal{L}'_0$ with respect to the orbital variation. The third term of $\mathbf{B^0}$ in Eq. (33), which includes B^0_{rv}, occurs due to the dependence of the multipliers and amplitudes in local basis on the coefficients $\mathbf{C}$, cf. Eq. (34). The derivative of a singlet doubles quantity (singles are not needed, *vide infra*), e.g., of the amplitude t^{ij}_{ab}, with respect to the orbital variation is

$$\left(\frac{\partial t^{ij}_{ab}}{\partial O_{pq}}\right)_{\mathbf{V}=0} = \left(\frac{\partial \left(Q_{ar} t^{ij}_{rt} Q_{bt}\right)}{\partial O_{pq}}\right)_{\mathbf{V}=0}$$

$$= 2\delta_{qa} C_{\mu p} S^{AO}_{\mu v} \delta_{vr} t^{ij}_{rt} Q_{bt}. \qquad (A1)$$

The derivative of $\mathcal{L}'_0$ with respect to the amplitudes $\mathbf{t}$ yields the equations for the multipliers and the derivative with respect to the Lagrange multipliers $\tilde{\lambda}^0$ the amplitude residual equations,

$$\left(\frac{\partial \mathcal{L}_0'}{\partial t_{ab}^{ij}}\right) = [\eta + \tilde{\lambda}^{\mathbf{0}}\mathbf{A}]_{ab}^{ij}$$

$$= (1 + \mathcal{P}_{ab}\mathcal{P}_{ij})\left\{ f_{ca}\tilde{\lambda}_{cb}^{ij,0} - \tilde{\lambda}_{ab}^{ik,0} f_{jk} \right.$$

$$\left. + \left(1 - \frac{1}{2}\mathcal{P}_{ij}\right)\left[(ia|jb) + \hat{G}_{ab}^{ij}(\tilde{\lambda}^0) + \tilde{\lambda}_a^{i,0}\hat{f}_{jb}\right]\right\},$$

$$\left(\frac{\partial \mathcal{L}_0'}{\partial \tilde{\lambda}_{ab}^{ij,0}}\right) = \Omega_{ab}^{ij} \qquad (A2)$$

$$= (1 + \mathcal{P}_{ab}\mathcal{P}_{ij})\left\{ \frac{1}{2}(ai\hat{|}bj) \right.$$

$$\left. + t_{ac}^{ij}f_{bc} - f_{ki}t_{ab}^{kj} \right\},$$

with

$$\eta = \frac{\partial E_0}{\partial t},$$

$$\hat{G}_{ab}^{ij}(\tilde{\lambda}) = \tilde{\lambda}_c^i(ca\hat{|}jb) - \tilde{\lambda}_a^k(ik\hat{|}jb). \qquad (A3)$$

The derivatives have to be calculated for the doubles parts only, which are restricted to pair lists and domains in the local basis (note that the amplitude and multiplier residual vectors only vanish in local basis within the pair domains, but not outside; consequently, they are non-zero in the canonical basis). The singles parts, on the other hand, are unrestricted, and the derivatives of $\mathcal{L}_0'$ with respect to singles amplitudes t_a^i or multipliers $\tilde{\lambda}_a^{i,0}$ are zero.

Thus, Eq. (34) can be written as

$$\sum_{\mu_i}\left[\left(\frac{\partial \mathcal{L}_0'}{\partial \tilde{\lambda}_{\mu_i}^0}\right)\left(\frac{\partial \tilde{\lambda}_{\mu_i}^0}{\partial O_{pq}}\right) + \left(\frac{\partial \mathcal{L}_0'}{\partial t_{\mu_i}}\right)\left(\frac{\partial t_{\mu_i}}{\partial O_{pq}}\right)\right]_{\mathbf{V}=0}$$

$$= 2C_{\mu p}S_{\mu\rho}^{AO}\delta_{\rho r}\left[t_{rt}^{ji}Q_{bt}\left(\frac{\partial \mathcal{L}_0'}{\partial t_{ab}^{ij}}\right) + \tilde{\lambda}_{rt}^{ji,0}Q_{bt}\left(\frac{\partial \mathcal{L}_0'}{\partial \tilde{\lambda}_{ab}^{ij,0}}\right)\right]$$

$$= C_{\mu p}S_{\mu\rho}^{AO}\delta_{\rho r}B_{rv}^0 C_{va}^v, \qquad (A4)$$

which is the starting point for the derivation of the working equations for $B_{r\mu}^0$. For these one obtains finally

$$B_{r\mu}^0 = -\hat{\tilde{M}}_{vr}\hat{C}_{v\mu} - 2M_{\mu r} + \bar{M}_{\mu r} + \check{M}_{\mu r}$$

$$+ \bar{\mathcal{D}}_{rt}^\xi(\lambda^0)f_{t\mu} + X(\lambda^0 T)_{jr}\hat{f}_{j\mu}$$

$$+ \left(X(\hat{f}_{it})_{jr}\tilde{\lambda}_u^{j,0} + M_{\rho r}\Lambda_{\rho k}^h\tilde{\lambda}_u^{k,0}\right.$$

$$\left. + \bar{d}_{ru}^D(f_{st}) - \bar{d}_{ru}^f\right)\delta_{uv}S_{v\mu}^{AO}. \qquad (A5)$$

The first two terms in Eq. (33) including $B_{\mu i}^0$ and $B_{\mu r}^0$ arise from the direct partial derivatives of $\mathcal{L}_0'$ for $q = i$ and $q = r$, respectively. The corresponding working equations are

$$B_{\mu i}^0 = 2f_{\mu r}t_r^i + \hat{f}_{\mu r}d_{ir}' + \hat{f}_{r\mu}d_{ri}' + \hat{f}_{k\mu}d_{ki}' + \hat{f}_{\mu k}d_{ik}'$$

$$+ 2g(\bar{d})_{\mu i} + 2g(d')_{\mu r}t_r^i + \bar{\mathcal{D}}_{ik}^\xi(\lambda^0)f_{k\mu}$$

$$+ (\mu r|Q)\left(\bar{V}_{ir}^Q + 4t_r^i b^Q - 2t_r^j \bar{c}_{ji}^Q\right)$$

$$- (\mu k\hat{|}Q)V_{ir}^Q S_{rr'}\tilde{\lambda}_{r'}^{k,0}$$

$$+ 2N_{\mu i} + d_{ik}'N_{\mu k} + \hat{\bar{N}}_{\mu i}$$

$$+ \tilde{\lambda}_{r'}^{i,0}S_{r'r}M_{\mu r} + \hat{\bar{M}}_{\mu r}S_{rr'}t_{r'}^i, \qquad (A6)$$

$$B_{\mu r}^0 = 2f_{k\mu}t_r^k + \hat{f}_{k\mu}d_{kr}' + \hat{f}_{\mu k}d_{rk}' + \hat{f}_{\mu s}d_{rs}' + \hat{f}_{s\mu}d_{sr}'$$

$$+ 2g(d'^\dagger)_{\mu k}t_r^k + \bar{\mathcal{D}}_{rs}^\xi(\lambda^0)f_{s\mu}$$

$$+ (k\mu|Q)\left(\bar{V}_{kr}^Q + 4t_r^k b^Q - 2t_r^j \bar{c}_{jk}^Q\right)$$

$$+ (s\mu\hat{|}Q)V_{kr}^Q\tilde{\lambda}_s^{k,0} + N_{\mu k}\tilde{\lambda}_r^{k,0} + \hat{\bar{N}}_{\mu k}t_r^k$$

$$- 2M_{\mu r} - \hat{\bar{M}}_{ra} + d_{sr}'S_{ss'}M_{\mu s'}. \qquad (A7)$$

The intermediates needed for calculating $B_{\mu i}^0$, $B_{\mu r}^0$, and $B_{r\mu}^0$ are

$$V_{ir}^Q = \tilde{t}_{rs}^{ij}c_Q^{js},$$

$$\hat{V}_{ir}^Q = \tilde{\lambda}_{rs}^{ij,0}\hat{c}_Q^{sj},$$

$$\bar{V}_{ir}^Q = \tilde{t}_{rs}^{ij}\left(\tilde{\lambda}_t^{j,0}\hat{c}_{ts}^P - S_{ss'}\tilde{\lambda}_{s'}^{k,0}\hat{c}_{jk}^P\right),$$

$$X(\lambda^0 T)_{ir} = \tilde{\lambda}_s^{j,0}S_{ss'}\tilde{t}_{s'r}^{ji}, \qquad X(\hat{f}_{jt})_{ir} = \hat{f}_{jt}\tilde{t}_{tr}^{ji},$$

$$d_{ij}' = -\tilde{\lambda}_r^{j,0}S_{rr'}t_{r'}^i, \qquad d_{rs}' = \tilde{\lambda}_r^{k,0}t_s^k,$$

$$d_{ir}' = t_r^k d_{ik}' + X(\lambda^0 T)_{ir}, \qquad d_{ri}' = \tilde{\lambda}_r^{i,0},$$

$$d_{ij}^{SCF} = 2\delta_{ij}, \qquad (A8)$$

$$d = d^{SCF} + \mathcal{D}^\xi(\lambda^0) + d',$$

$$d_{ru}^D(f_{st}) = 2\tilde{\lambda}_{rs}^{ji,0}f_{st}t_{tu}^{ij},$$

$$d_{ru}^f = 2\tilde{\lambda}_{rt'}^{ji,0}S_{t't}\left(f_{ki}t_{tu}^{kj} + f_{kj}t_{tu}^{ik}\right),$$

$$g(d)_{pq} = ((pq|rs) - 0.5(ps|rq))d_{rs},$$

$$b^Q = c_{ir}^Q t_r^i, \qquad \bar{c}_{ij}^Q = c_{ir}^Q t_r^j,$$

$$\hat{C}_{\mu v} = \delta_{\mu v} - L_{\mu k}t_r^k\delta_{r\rho}S_{\rho v}^{AO},$$

a bar indicates symmetrized densities, e.g., $\bar{d} = d + d^\dagger$. All $\hat{f}$ are dressed only internally (cf. Eq. (13)), the density $\mathcal{D}^\xi$ was already defined in Eq. (52). $\mathbf{g}(d)$ is also constructed by employing density fitting, i.e., according to Eq. (60) in Ref. 40. The intermediates including half transformed integrals are

$$(i\mu|Q) = (v\mu|Q)\Lambda_{vi}^p, \qquad (\mu i\hat{|}Q) = (\mu v|Q)\Lambda_{vi}^h,$$

$$(\mu r|Q) = (\mu v|Q)\Lambda_{vr}^h, \qquad (r\mu\hat{|}Q) = (v\mu|Q)\Lambda_{vr}^p,$$

$$M_{\mu r} = -V_{kr}^Q(k\mu|Q), \qquad N_{\mu i} = V_{kr}^Q(\mu r|Q), \quad (A9)$$

$$\hat{M}_{\mu r} = -2\hat{V}_{kr}^Q(\mu k\hat{|}Q), \qquad \hat{N}_{\mu i} = 2\hat{V}_{kr}^Q(r\mu\hat{|}Q),$$

$$\bar{M}_{\mu r} = \bar{V}_{kr}^Q(Q\hat{|}\mu k), \qquad \check{M}_{\mu r} = V_{kr}^Q\tilde{\lambda}_s^{k,0}(Q\hat{|}s\mu).$$

APPENDIX B: WORKING EQUATIONS FOR SINGLET EXCITED STATES

Analogously to the ground state the terms including $B_{\mu i}^f$ and $B_{\mu r}^f$ in Eq. (41) arise from the direct partial derivatives with respect to O_{pq} for $q = i$ and $q = r$, respectively. The term including B_{rv}^f has its origin in the dependence of the doubles amplitudes, eigenvectors, and Lagrange multipliers on the orbital variation (cf. Eqs. (34) and (A1)). The derivatives with respect to the Lagrange multipliers $\tilde{\boldsymbol{\lambda}}^{\mathbf{f}}$ yield the amplitude equations, with respect to the amplitudes $\mathbf{t}$ the equations for the multipliers, with respect to the right eigenvector $\mathbf{R^f}$ the left eigenvalue equation, and with respect to the left eigenvector $\tilde{\mathbf{L}}^{\mathbf{f}}$ the right eigenvalue equation,

$$\mathcal{L}'_f = \tilde{\mathbf{L}}\mathbf{A}\mathbf{R} + \tilde{\boldsymbol{\lambda}}^{\mathbf{f}}\Omega - \omega[\tilde{\mathbf{L}}\mathbf{M}\mathbf{R} - 1],$$

$$\left(\frac{\partial \mathcal{L}'_f}{\partial t_{ab}^{ij}}\right) = [\tilde{\mathbf{L}}\mathbf{B}\mathbf{R} + \tilde{\boldsymbol{\lambda}}^{\mathbf{f}}\mathbf{A}]_{ab}^{ij}$$

$$= (1 + \mathcal{P}_{ab}\mathcal{P}_{ij})\Big\{ f_{ca}\tilde{\lambda}_{cb}^{ij,f} - \tilde{\lambda}_{ab}^{ik,f} f_{jk}$$

$$+ \left(1 - \frac{1}{2}\mathcal{P}_{ij}\right)\big[-\tilde{L}_b^k R_c^k(jc|ia)$$

$$+ 2\tilde{L}_a^i R_c^k(jb|kc) - \tilde{L}_a^i R_c^k(jc|kb) - \tilde{L}_c^i R_c^k(ka|jb)$$

$$+ \hat{G}_{ab}^{ij}(\tilde{\lambda}^f) + \tilde{\lambda}_a^{i,f} \hat{f}_{jb}\big]\Big\},$$

$$\left(\frac{\partial \mathcal{L}'_f}{\partial \tilde{\lambda}_{ab}^{ij,f}}\right) = \Omega_{ab}^{ij}$$

$$= (1 + \mathcal{P}_{ab}\mathcal{P}_{ij})\left\{ \frac{1}{2}(ai\check{|}bj) + t_{ac}^{ij} f_{bc} - f_{ki}t_{ab}^{kj} \right\},$$

$$\left(\frac{\partial \mathcal{L}'_f}{\partial R_{ab}^{ij}}\right) = [\tilde{\mathbf{L}}\mathbf{A} - \omega\tilde{\mathbf{L}}\mathbf{M}]_{ab}^{ij} \qquad (B1)$$

$$= (1 + \mathcal{P}_{ab}\mathcal{P}_{ij})\Big\{ \tilde{L}_{ac}^{ij} f_{cb} - \tilde{L}_{ab}^{ik} f_{jk} - \frac{1}{2}\omega\tilde{L}_{ab}^{ij}$$

$$+ (1 - \frac{1}{2}\mathcal{P}_{ij})[\tilde{L}_a^i \hat{f}_{jb} + \tilde{L}_c^i(ca\check{|}jb) - \tilde{L}_a^k(ik\check{|}jb)]\Big\},$$

$$\left(\frac{\partial \mathcal{L}'_f}{\partial \tilde{L}_{ab}^{ij}}\right) = [\mathbf{A}\mathbf{R} - \omega\mathbf{M}\mathbf{R}]_{ab}^{ij}$$

$$= (1 + \mathcal{P}_{ab}\mathcal{P}_{ij})\Big[(ac\check{|}bj)R_c^i - (ki\check{|}bj)R_a^k$$

$$+ f_{ac}R_{cb}^{ij} - R_{ab}^{ik} f_{kj} - \frac{1}{2}\omega R_{ab}^{ij}\Big],$$

with

$$B_{\mu_i \sigma_k \nu_j} = \frac{\partial A_{\mu_i \nu_j}}{\partial t_{\sigma_k}}. \qquad (B2)$$

Adapting Eq. (A4) for excited states yields the working equation for the intermediate $B_{r\mu}^f$ in Eq. (41),

$$B_{r\mu}^f = \big(X(\lambda^f T)_{jr} + d_{jr}^{LR2}\big)\hat{f}_{j\mu} + \big(\bar{\mathcal{D}}_{tr}^\xi(\lambda^f) + \bar{\mathcal{D}}_{tr}^\eta\big)f_{t\mu}$$

$$+ (j\mu|Q)\Big[V_{kr}^Q d_{jk}^L + 2X(LT)_{jr}{}^R b^Q$$

$$- X(LT)_{kr}{}^R \bar{c}_{kj}^Q\Big]$$

$$+ (j\mu\check{|}Q)V_{jr}^Q + (j\mu\hat{\check{|}}Q)^R V_{jr}^Q - \bar{M}_{\mu r} - {}^{LR\bar{V}}M_{\mu r}$$

$$- \hat{\bar{M}}_{vr}\hat{C}_{v\mu} - {}^{LW}M_{vr}\hat{C}_{v\mu} - \tilde{M}_{vr}\hat{C}_{v\mu}$$

$$+ \Big\{ -\bar{d}_{ru}^f - \bar{d}_{ru}^{f(LR)} + \bar{d}_{ru}^D(f_{st}) + \bar{d}_{ru}^{D(LR)}(f_{st})$$

$$- \omega\bar{\mathcal{D}}_{ru}^\eta + X(\hat{f}_{it})_{jr}\tilde{\lambda}_u^{j,f} + {}^R X(\hat{f}_{it})_{jr}\tilde{L}_u^j$$

$$+ 2\tilde{L}_u^j V_{jr}^Q(ks|Q)R_s^k - \tilde{L}_u^j\tilde{t}_{rs}^{ji}(ks|Q)^R\bar{c}_{ik}^Q$$

$$+ M_{\rho r}P_{\rho t}d_{ut}^L + {}^R M_{\rho r}\Lambda_{\rho k}^h\tilde{L}_u^k$$

$$+ {}^{LW}M_{\rho r}L_{\rho k}R_u^k + M_{\rho r}\Lambda_{\rho k}^h\tilde{\lambda}_u^{k,f}\Big\}\delta_{uv}S_{v\mu}^{AO}, \quad (B3)$$

while $B_{\mu i}^f$ and $B_{\mu r}^f$ are obtained from the direct partial derivatives of $\mathcal{L}'_f$ with respect to the orbital variation for $q = i$ and $q = r$, respectively,

$$B_{\mu i}^f = \hat{f}_{\mu k}\big(d_{ik}^L + d'_{ik}\big) + \hat{f}_{k\mu}\big(d_{ki}^L + d'_{ki}\big) + \hat{f}_{s\mu}d'_{si}$$

$$+ \hat{f}_{\mu s}\big(d_{is}^L + d_{is}^{LR2} + d'_{is}\big) + f_{k\mu}\big(\bar{\mathcal{D}}_{ik}^\xi(\lambda^f) + \bar{\mathcal{D}}_{ik}^\eta\big)$$

$$+ 2g\big(\bar{d}^L + \bar{d}^{LR2} + \bar{\mathcal{D}}^\xi(\lambda^f) + \bar{\mathcal{D}}^\eta + \bar{d}'\big)_{\mu i}$$

$$+ 2g(d^L + d^{LR2} + d')_{\mu s}t_s^i$$

$$+ (k\mu|Q)\big[-{}^{LR}\bar{c}_{ik}^Q - 2^L V_{ir}^Q S_{rr'}R_{r'}^k\big]$$

$$+ (\mu k\check{|}Q)\big[-{}^{LR}\bar{c}_{ki}^Q - \tilde{L}_r^k S_{rr'}{}^R V_{ir'}^Q$$

$$+ 2d_{ik}^{Lt}{}^R b^Q - V_{is}^Q S_{ss'}\tilde{\lambda}_{s'}^{k,f}\big]$$

$$+ (\mu i\check{|}Q)[2^L b^Q + 2^X b^Q]$$

$$+ (\mu l\check{|}Q)\big[-d_{ik}^{Lt}\hat{c}_{l\bar{k}}^Q - {}^X\bar{c}_{li}^Q - \tilde{L}_s^l S_{ss'}V_{is'}^Q\big]$$

$$+ 2(i\mu\hat{\check{|}}Q)^R b^Q$$

$$+ (\mu r|Q)\big[\bar{V}_{ir}^Q - X(LT)_{lr}{}^R\bar{c}_{li}^Q + 2X(LT)_{ir}{}^R b^Q\big]$$

$$+ {}^{LR\bar{V}}N_{\mu i} + {}^{LW}N_{\mu i} + \hat{\bar{N}}_{\mu i} + \big(d_{ik}^L + d'_{ik}\big)N_{\mu k}$$

$$+ d_{ik}^{Lt}{}^R N_{\mu k} + \tilde{M}_{\mu s}S_{ss'}t_{s'}^i$$

$$+ {}^{LW}M_{\mu s}S_{ss'}t_{s'}^i + {}^L M_{\mu s}S_{ss'}R_{s'}^i + M_{\mu s}S_{ss'}\tilde{\lambda}_{s'}^{i,f}$$

$$+ \hat{\bar{M}}_{\mu s}S_{ss'}t_{s'}^i + {}^R M_{\mu s}S_{ss'}\tilde{L}_{s'}^i, \qquad (B4)$$

$$B_{\mu r}^f = \hat{f}_{k\mu}\big(d_{kr}^L + d'_{kr} + d_{kr}^{LR2}\big) + \hat{f}_{\mu k}d'_{rk}$$

$$+ \hat{f}_{s\mu}\big(d_{sr}^L + d'_{sr}\big) + \hat{f}_{\mu s}\big(d_{rs}^L + d'_{rs}\big)$$

$$+ f_{\mu s}\big(\bar{\mathcal{D}}_{rs}^\xi(\lambda^f) + \bar{\mathcal{D}}_{rs}^\eta\big)$$

$$+ 2g(d^L + d^{LR2} + d')_{k\mu}t_r^k$$

$$+ (i\mu|Q)\big[d_{ik}^L V_{kr}^Q - 2^L V_{ks}^Q S_{ss'}R_{s'}^i t_r^k + \bar{V}_{ir}^Q$$

$$+ 2^L b^Q R_r^i - {}^{LR}\bar{c}_{ki}^Q t_r^k$$

$$+ 2^X b^Q R_r^i - {}^X\bar{c}_{li}^Q R_r^l$$

$$+ 2X(LT)_{ir}{}^R b^Q - X(LT)_{lr}{}^R\bar{c}_{li}^Q\big]$$

$$+ 2(\mu k\hat{\rceil}Q)\tilde{L}_r^k{}^R b^Q - (\mu i\tilde{\rceil}Q)\tilde{L}_r^k\hat{c}_{i\bar{k}}^Q + (i\mu\breve{\rceil}Q)V_{ir}^Q$$

$$+ (k\mu\hat{\tilde{\rceil}}Q)\big[{}^R V_{kr}^Q - \hat{c}_{i\bar{k}}^Q R_r^i + 2t_r^k{}^R b^Q\big]$$

$$+ ({}^{LW}N_{\mu k} + \hat{\tilde{N}}_{\mu k})t_r^k + {}^R N_{\mu k}\tilde{L}_r^k + {}^L N_{\mu k}R_r^k$$

$$+ N_{\mu k}\tilde{\lambda}_r^{k,f} - {}^{LR\bar{V}}M_{\mu r} - {}^{LW}M_{\mu r} - \hat{\tilde{M}}_{\mu r} - \tilde{M}_{\mu r}$$

$$+ M_{\mu s}S_{ss'}d_{s'r}^L + {}^R M_{\mu s}S_{ss'}d_{s'r}^{Lt}$$

$$+ M_{\mu s}S_{ss'}d'_{s'r}. \tag{B5}$$

$\hat{f}$ is again dressed only internally. The intermediates including 3-index quantities are

$$\begin{aligned} {}^R b^Q &= c_{ir}^Q R_r^i, & {}^R\bar{c}_{ij}^Q &= c_{ir}^Q R_r^j, \\[4pt] {}^X b^Q &= c_{ir}^Q X(LT)_{ir}, & {}^X\bar{c}_{ij}^Q &= c_{ir}^Q X(LT)_{jr}, \\[4pt] {}^L b^Q &= \hat{c}_{ri}^Q \tilde{L}_r^i, & {}^{LR}\bar{c}_{ij}^Q &= \tilde{L}_s^i \hat{c}_{sr}^Q R_r^j, \\[4pt] V_{ir}^Q &= \tilde{t}_{rs}^{ij}c_{js}^Q, & \hat{V}_{ir}^Q &= \tilde{\lambda}_{rs}^{ij,f}\hat{c}_{sj}^Q, \\[4pt] {}^R V_{ir}^Q &= \tilde{R}_{rs}^{ij}c_{js}^Q, & {}^L V_{ir}^Q &= \tilde{L}_{rs}^{ij}\hat{c}_{sj}^Q, \end{aligned} \tag{B6}$$

$${}^L W_{ir}^Q = \tilde{L}_{rs}^{ij}\big(R_t^j\hat{c}_{st}^Q - S_{ss'}R_s^k\hat{c}_{kj}^Q\big),$$

$${}^{LR}\bar{V}_{ir}^Q = \tilde{R}_{rs}^{ij}\big(\tilde{L}_t^j\hat{c}_{ts}^Q - S_{ss'}\tilde{L}_{s'}^k\hat{c}_{jk}^Q\big),$$

$$\hat{B}_{ir}^Q = \tilde{\lambda}_s^{i,f}\hat{c}_{sr}^Q - S_{rr'}\tilde{\lambda}_{r'}^{k,f}\hat{c}_{ik}^Q,$$

$$\hat{B}'^Q_{ir} = d_{ki}^L c_{kr}^Q - S_{rr'}d_{r's}^L c_{is}^Q,$$

$$\bar{V}_{ir}^Q = \tilde{t}_{rs}^{ij}\big(\hat{B}_{js}^Q + \hat{B}'^Q_{js}\big).$$

The intermediates including half-transformed integrals are

$$(\mu i\tilde{\rceil}Q) = (\mu s|Q)R_s^i, \qquad (i\mu\hat{\rceil}Q) = (s\mu\hat{\rceil}Q)\tilde{L}_s^i,$$

$$(i\mu\breve{\rceil}Q) = (s\mu\hat{\rceil}Q)\tilde{\lambda}_s^{i,f}, \qquad \tilde{M}_{\mu r} = -2^L V_{kr}^Q(\mu k\tilde{\rceil}Q),$$

$$M_{\mu r} = -(k\mu|Q)V_{kr}^Q, \qquad N_{\mu i} = V_{is}^Q(\mu s|Q),$$

$${}^R M_{\mu r} = -(k\mu|Q)^R V_{kr}^Q, \qquad {}^R N_{\mu i} = {}^R V_{is}^Q(\mu s|Q),$$

$${}^{LR\bar{V}}M_{\mu r} = -(k\mu|Q)^{LR}\bar{V}_{kr}^Q, \quad {}^{LR\bar{V}}N_{\mu i} = {}^{LR}\bar{V}_{is}^Q(\mu s|Q), \tag{B7}$$

$${}^L M_{\mu r} = -2(\mu k\hat{\rceil}Q)^L V_{kr}^Q, \qquad {}^L N_{\mu i} = 2^L V_{is}^Q(s\mu\hat{\rceil}Q),$$

$${}^{LW}M_{\mu r} = -2(\mu k\hat{\rceil}Q)^L W_{kr}^Q, \quad {}^{LW}N_{\mu i} = 2^L W_{is}^Q(s\mu\hat{\rceil}Q),$$

$$\hat{\tilde{M}}_{\mu r} = -2(\mu k\hat{\rceil}Q)\hat{V}_{kr}^Q, \qquad \hat{\tilde{L}}_{\mu i} = 2\hat{V}_{is}^Q(s\mu\hat{\rceil}Q),$$

$$\bar{M}_{\mu r} = -(k\mu|Q)\bar{V}_{kr}^Q.$$

The densities $\mathcal{D}^\xi$ and $\mathcal{D}^\eta$ were defined in Eqs. (52) and (53), the remaining intermediates are

$$X(LT)_{ir} = \tilde{L}_s^j S_{ss'}\tilde{t}_{s'r}^{ji}, \qquad X(\lambda^f T)_{ir} = \tilde{\lambda}_s^{j,f}S_{ss'}\tilde{t}_{s'r}^{ji},$$

$$d'_{ij} = -\tilde{\lambda}_s^{j,f}S_{ss'}t_{s'}^i, \qquad d'_{ri} = \tilde{\lambda}_r^{i,f},$$

$$d'_{ir} = t_r^k d'_{ik} + X(\lambda^f T)_{ir}, \quad d'_{rs} = \tilde{\lambda}_r^{k,f}t_s^k,$$

$$d_{ij}^{Lt} = -\tilde{L}_s^j S_{ss'}t_{s'}^i, \qquad d_{rs}^{Lt} = \tilde{L}_r^k t_s^k,$$

$$d_{ij}^L = -\tilde{L}_s^j S_{ss'}R_{s'}^i, \qquad d_{rs}^L = \tilde{L}_r^k R_s^k,$$

$$d_{ir}^L = -\tilde{L}_s^k S_{ss'}\big(R_{s'}^i t_r^k + R_r^k t_{s'}^i\big), \tag{B8}$$

$$d_{ir}^{LR2} = \tilde{L}_s^k S_{ss'}\tilde{R}_{s'r}^{ji},$$

$$d_{ru}^f = 2\tilde{\lambda}_{rt'}^{ji,f}S_{t't}\big(f_{ki}t_{tu}^{kj} + f_{kj}t_{tu}^{ik}\big),$$

$$d_{ru}^{f(LR)} = 2\tilde{L}_{rt'}^{ji}S_{t't}\big(f_{ki}R_{tu}^{kj} + f_{kj}R_{tu}^{ik}\big),$$

$$d_{ru}^D(f) = 2\tilde{\lambda}_{rs}^{ji,f}f_{st}t_{tu}^{ij},$$

$$d_{ru}^{D(LR)}(f) = 2\tilde{L}_{rs}^{ji}f_{st}R_{tu}^{ij},$$

$${}^R X(\hat{f}_{it})_{jr} = \hat{f}_{it}\tilde{R}_{tr}^{ij}.$$

APPENDIX C: WORKING EQUATIONS FOR TRIPLET EXCITED STATES

Analogously to singlet excited states the dependence of Lagrange multipliers, amplitudes, left and right eigenvector on the MO coefficients yields the third term in Eq. (41) for triplet states. The derivatives of the plus and minus combinations of the left and right eigenvector have to be

calculated,

$$\left(\frac{\partial \mathcal{L}'_f}{\partial t^{ij}_{ab}}\right) = (1 + \mathcal{P}_{ab}\mathcal{P}_{ij})\left\{\frac{1}{2}\tilde{L}^j_a(kb|ic)R^k_c\right.$$

$$+ f_{ca}\tilde{\lambda}^{ij,f}_{cb} - \tilde{\lambda}^{kj,f}_{ab}f_{ik}$$

$$+ \left(1 - \frac{1}{2}\mathcal{P}_{ij}\right)\left[\hat{G}^{ij}_{ab}(\tilde{\lambda}^f) + \tilde{\lambda}^{i,f}_a \hat{f}_{jb}\right.$$

$$\left.\left. - \tilde{L}^i_c(jb|ka)R^k_c - \tilde{L}^k_a(jb|ic)R^k_c\right]\right\},$$

$$\left(\frac{\partial \mathcal{L}'_f}{\partial \tilde{\lambda}^{ij,f}_{ab}}\right) = (1 + \mathcal{P}_{ab}\mathcal{P}_{ij})\left\{\frac{1}{2}(ai\hat{|}bj) + t^{ij}_{ac}f_{bc} - f_{ki}t^{kj}_{ab}\right\},$$

$$\left(\frac{\partial \mathcal{L}'_f}{\partial \overset{(+)}{R}{}^{ij}_{ab}}\right) = \frac{1}{4}(1 + \mathcal{P}_{ab}\mathcal{P}_{ij})(1 - \mathcal{P}_{ij})$$

$$\left\{2\tilde{L}^i_a\hat{f}_{jb} - 2\tilde{L}^k_a(jb\hat{|}ik) + 2\tilde{L}^i_c(jb\hat{|}ca)\right.$$

$$\left. + f_{cb}\overset{(+)}{\tilde{L}}{}^{ij}_{ac} - f_{jk}\overset{(+)}{\tilde{L}}{}^{ik}_{ab} - \frac{1}{2}\omega\overset{(+)}{\tilde{L}}{}^{ij}_{ab}\right\},$$

$$\left(\frac{\partial \mathcal{L}'_f}{\partial \overset{(-)}{R}{}^{ij}_{ab}}\right) = \frac{1}{2}(1 - \mathcal{P}_{ab}\mathcal{P}_{ij}) \tag{C1}$$

$$\left\{2\tilde{L}^i_a\hat{f}_{jb} - 2\tilde{L}^k_a(jb\hat{|}ik) + 2\tilde{L}^i_c(jb\hat{|}ca)\right.$$

$$\left. + 2f_{cb}\overset{(-)}{\tilde{L}}{}^{ij}_{ac} - 2f_{jk}\overset{(-)}{\tilde{L}}{}^{ik}_{ab} - \omega\overset{(-)}{\tilde{L}}{}^{ij}_{ab}\right\},$$

$$\left(\frac{\partial \mathcal{L}'_f}{\partial \tilde{L}^{ij}_{ab}}\right) = \frac{1}{4}(1 + \mathcal{P}_{ab}\mathcal{P}_{ij})(1 - \mathcal{P}_{ij})$$

$$\left\{(ac\hat{|}bj)R^i_c - (ki\hat{|}bj)R^k_a\right.$$

$$\left. + f_{bc}\overset{(+)}{R}{}^{ij}_{ac} - f_{kj}\overset{(+)}{R}{}^{ik}_{ab} - \frac{1}{2}\omega\overset{(+)}{R}{}^{ij}_{ab}\right\},$$

$$\left(\frac{\partial \mathcal{L}'_f}{\partial \tilde{L}^{ij}_{ab}}\right) = \frac{1}{2}(1 - \mathcal{P}_{ab}\mathcal{P}_{ij})$$

$$\left\{(ac\hat{|}bj)R^i_c - (ki\hat{|}bj)R^k_a\right.$$

$$\left. + 2f_{bc}\overset{(-)}{R}{}^{ij}_{ac} - 2f_{kj}\overset{(-)}{R}{}^{ik}_{ab} - \omega\overset{(-)}{R}{}^{ij}_{ab}\right\}.$$

These derivatives contribute to the third term of Eq. (41) for excited triplet states in analogy to Eq. (34) for the ground state case. For the plus combination of a triplet doubles quantity,

e.g., the right eigenvector $\overset{(+)}{R}{}^{ij}_{ab}$, the derivative is then calculated as

$$\left[\left(\frac{\partial \mathcal{L}'_f}{\partial \overset{(+)}{R}{}^{ij}_{ab}}\right)\left(\frac{\partial \overset{(+)}{R}{}^{ij}_{ab}}{\partial O_{pq}}\right)\right]_{\mathbf{V}=0}$$

$$= \delta_{qa}C_{p\mu}S^{AO}_{\mu v}\delta_{vr}\left(\left(\frac{\partial \mathcal{L}'_f}{\partial \overset{(+)}{R}{}^{ij}_{\rho s}}\right) - \left(\frac{\partial \mathcal{L}'_f}{\partial \overset{(+)}{R}{}^{ij}_{s\rho}}\right)\right)\overset{(+)}{R}{}^{ij}_{rs}C_{\rho a}$$

$$= 2\delta_{qa}C_{p\mu}S^{AO}_{\mu v}\delta_{vr}\left(\frac{\partial \mathcal{L}'_f}{\partial \overset{(+)}{R}{}^{ij}_{\rho s}}\right)\overset{(+)}{R}{}^{ij}_{rs}C_{\rho a}, \tag{C2}$$

and for a triplet quantity $\overset{(-)}{R}{}^{ij}_{ab}$ as

$$\left[\left(\frac{\partial \mathcal{L}}{\partial \overset{(-)}{R}{}^{ij}_{ab}}\right)\left(\frac{\partial \overset{(-)}{R}{}^{ij}_{ab}}{\partial O_{pq}}\right)\right]_{\mathbf{V}=0}$$

$$= \delta_{qa}C_{p\mu}S^{AO}_{\mu v}\delta_{vr}\left(\left(\frac{\partial \mathcal{L}'_f}{\partial \overset{(-)}{R}{}^{ij}_{\rho s}}\right) - \left(\frac{\partial \mathcal{L}'_f}{\partial \overset{(-)}{R}{}^{ji}_{s\rho}}\right)\right)\overset{(-)}{R}{}^{ij}_{rs}C_{\rho a}$$

$$= 2\delta_{qa}C_{p\mu}S^{AO}_{\mu v}\delta_{vr}\left(\frac{\partial \mathcal{L}'_f}{\partial \overset{(-)}{R}{}^{ij}_{\rho s}}\right)\overset{(-)}{R}{}^{ij}_{rs}C_{\rho a}. \tag{C3}$$

From this starting point the intermediate $B^f_{r\mu}$ in Eq. (41) is in local basis obtained as

$$B^f_{r\mu} = \left(X(\lambda^f T)_{jr} + d^{LR2}_{jr}\right)\hat{f}_{j\mu} + \left(\bar{\mathcal{D}}^{\xi}_{tr}(\lambda^f) + \bar{\mathcal{D}}^{\eta}_{tr}\right)f_{t\mu}$$

$$+ (j\mu|Q)\left[V^Q_{kr}d^L_{jk} - X'(LT)_{kr}{}^R\bar{c}^Q_{kj}\right]$$

$$+ (j\mu\breve{|}Q)V^Q_{jr} + (j\mu\hat{\breve{|}}Q){}^RV^Q_{jr} - \bar{M}_{\mu r} - {}^{LR\bar{V}}M_{\mu r}$$

$$- \hat{\bar{M}}_{vr}\hat{C}_{v\mu} - \frac{1}{4}{}^{LW}M_{vr}\hat{C}_{v\mu} - \frac{1}{4}\tilde{M}_{vr}\hat{C}_{v\mu}$$

$$+ \left\{-\bar{d}^f_{ru} - \bar{d}^{f(LR)}_{ru} + \bar{d}^D_{ru}(f_{st}) + \bar{d}^{D(LR)}_{ru}(f_{st})\right.$$

$$- \omega\bar{\mathcal{D}}^{\eta}_{ru} + X(\hat{f}_{it})_{jr}\tilde{\lambda}^{j,f}_u + {}^RX(\hat{f}_{it})_{jr}\tilde{L}^j_u$$

$$+ M_{\rho r}P_{\rho t}d^L_{ut} + {}^RM_{\rho r}\Lambda^h_{\rho k}\tilde{L}^k_u$$

$$+ \frac{1}{4}{}^LM_{\rho r}L_{\rho k}R^k_u + M_{\rho r}\Lambda^h_{\rho k}\tilde{\lambda}^{k,f}_u$$

$$\left. + \tilde{L}^i_u t^{ji}_{rs}(ks|Q){}^R\bar{c}^Q_{jk}\right\}\delta_{uv}S^{AO}_{v\mu}. \tag{C4}$$

The direct partial derivatives yield the quantities $B_{\mu i}^f$ and $B_{\mu r}^f$, which are calculated as

$$B_{\mu i}^f = \hat{f}_{\mu k}(d_{ik}^L + d'_{ik}) + \hat{f}_{k\mu}(d_{ki}^L + d'_{ki}) + \hat{f}_{s\mu}d'_{si}$$

$$+ \hat{f}_{\mu s}(d_{is}^L + d_{is}^{LR2} + d'_{is}) + f_{k\mu}(\bar{\mathcal{D}}_{ik}^\xi(\lambda^f) + \bar{\mathcal{D}}_{ik}^\eta)$$

$$+ 2g(\bar{d}^L + \bar{d}^{LR2} + \bar{\mathcal{D}}^\xi(\lambda^f) + \bar{\mathcal{D}}^\eta + \bar{d}')_{\mu i}$$

$$+ 2g(d^L + d^{LR2} + d')_{\mu s}t_s^i$$

$$+ (k\mu|Q)\left[-{}^{LR}\bar{c}_{ik}^Q - \frac{1}{2}{}^L V_{ir}^Q S_{rr'}R_{r'}^k\right]$$

$$+ (\mu k\hat{|}Q)\left[-{}^{LR}\bar{c}_{ki}^Q - \tilde{L}_r^k S_{rr'}{}^R V_{ir'}^Q - V_{is}^Q S_{ss'}\tilde{\lambda}_{s'}^{k,f}\right]$$

$$+ (\mu l\tilde{|}Q)\left[-d_{ik}^{Lt}\hat{c}_{l\bar{k}}^Q - {}^{X'}\bar{c}_{li}^Q - \tilde{L}_s^l S_{ss'}V_{is'}^Q\right]$$

$$+ (\mu r|Q)\left[\bar{V}_{ir}^Q - X'(LT)_{lr}{}^R\bar{c}_{li}^Q\right]$$

$$+ {}^{LR\bar{V}}N_{\mu i} + \frac{1}{4}{}^{LW}N_{\mu i} + \hat{\bar{N}}_{\mu i}$$

$$+ (d_{ik}^L + d'_{ik})N_{\mu k} + d_{ik}^{Lt}{}^R N_{\mu k}$$

$$+ \frac{1}{4}{}^{LW}M_{\mu s}S_{ss'}t_{s'}^i + \frac{1}{4}{}^L M_{\mu s}S_{ss'}R_{s'}^i + M_{\mu s}S_{ss'}\tilde{\lambda}_{s'}^{i,f}$$

$$+ \hat{\bar{M}}_{\mu s}S_{ss'}t_{s'}^i + {}^R M_{\mu s}S_{ss'}\tilde{L}_{s'}^i + \frac{1}{4}\tilde{M}_{\mu s}S_{ss'}t_{s'}^i, \quad (C5)$$

$$B_{\mu r}^f = \hat{f}_{k\mu}(d_{kr}^L + d'_{kr} + d_{kr}^{LR2}) + \hat{f}_{\mu k}d'_{rk} + \hat{f}_{s\mu}(d_{sr}^L + d'_{sr})$$

$$+ \hat{f}_{\mu s}(d_{rs}^L + d'_{rs}) + f_{\mu s}(\bar{\mathcal{D}}_{rs}^\xi(\lambda^f) + \bar{\mathcal{D}}_{rs}^\eta)$$

$$+ 2g(d^L + d^{LR2} + d')_{k\mu}t_r^k$$

$$+ (i\mu|Q)\left[d_{ik}^L V_{kr}^Q - \frac{1}{2}{}^L V_{ks}^Q S_{ss'}R_{s'}^i t_r^k + \bar{V}_{ir}^Q - {}^{LR}\bar{c}_{ki}^Q t_r^k\right.$$

$$\left. - {}^{X'}\bar{c}_{li}^Q R_r^l - X'(LT)_{lr}{}^R\bar{c}_{li}^Q\right]$$

$$- (\mu i\tilde{|}Q)\tilde{L}_r^k\hat{c}_{i\bar{k}}^Q + (i\mu\breve{|}Q)V_{ir}^Q$$

$$+ (k\mu\hat{\tilde{|}}Q)\left[{}^R V_{kr}^Q - \hat{c}_{i\bar{k}}^Q R_r^i\right]$$

$$+ \left(\frac{1}{4}{}^{LW}N_{\mu k} + \hat{\bar{N}}_{\mu k}\right)t_r^k + {}^R N_{\mu k}\tilde{L}_r^k + \frac{1}{4}{}^L N_{\mu k}R_r^k$$

$$+ N_{\mu k}\tilde{\lambda}_r^{k,f} - {}^{LR\bar{V}}M_{\mu r} - \frac{1}{4}{}^{LW}M_{\mu r} - \frac{1}{4}\tilde{M}_{\mu r} - \hat{\bar{M}}_{\mu r}$$

$$+ M_{\mu s}S_{ss'}d_{s'r}^L + {}^R M_{\mu s}S_{ss'}d_{s'r}^{Lt} + M_{\mu s}S_{ss'}d'_{s'r}. \quad (C6)$$

The intermediates different from those already defined for singlet excited states (Appendix B) are

$$\bar{R}_{rs}^{ij} = 2\big(\overset{(+)}{R_{rs}^{ij}} + \overset{(-)}{R_{rs}^{ij}}\big), \qquad \bar{L}_{rs}^{ij} = 2\big(\overset{(+)}{\tilde{L}_{rs}^{ij}} + \overset{(-)}{\tilde{L}_{rs}^{ij}}\big),$$

$$^R V_{ir}^Q = \bar{R}_{rs}^{ij}c_{js}^Q, \qquad {}^L V_{ir}^Q = \bar{L}_{rs}^{ij}\hat{c}_{sj}^Q,$$

$$^L W_{ir}^Q = \bar{L}_{sr}^{ji}\big(R_t^j\hat{c}_{st}^Q - S_{ss'}R_{s'}^k\hat{c}_{kj}^Q\big),$$

$$^{LR}\bar{V}_{ir}^Q = \bar{R}_{sr}^{ji}\big(\tilde{L}_t^j\hat{c}_{ts}^Q - S_{ss'}\tilde{L}_{s'}^k\hat{c}_{jk}^Q\big),$$

$$X'(LT)_{ir} = -\tilde{L}_s^j S_{ss'}t_{s'r}^{ij}, \qquad {}^{X'}\bar{c}_{ij}^Q = c_{ir}^Q X'(LT)_{jr},$$

$$^R X(\hat{f}_{it})_{jr} = \bar{R}_{rt}^{ji}\hat{f}_{it}, \qquad (C7)$$

$$d_{ir}^{LR2} = \tilde{L}_s^j S_{ss'}\bar{R}_{s'r}^{ji},$$

$$d_{ru}^f = 2\tilde{\lambda}_{rt'}^{ji,f}S_{t't}\big(f_{ki}t_{tu}^{kj} + f_{kj}t_{tu}^{ik}\big),$$

$$d_{ru}^{f(LR)} = \tilde{L}_{rt'}^{ji}S_{t't}\big(f_{ki}\overset{(+)}{R_{tu}^{kj}} + f_{kj}\overset{(+)}{R_{tu}^{ik}}\big)$$

$$- 2\tilde{L}_{rt'}^{ji}S_{t't}\big(f_{ki}\overset{(-)}{R_{tu}^{kj}} + f_{kj}\overset{(-)}{R_{tu}^{ik}}\big),$$

$$d_{ru}^D(f) = 2\tilde{\lambda}_{rs}^{ji,f}f_{st}t_{tu}^{ij},$$

$$d_{ru}^{D(LR)}(f) = \tilde{L}_{rs}^{ji}f_{st}\overset{(+)}{R_{tu}^{ij}} - 2\tilde{L}_{rs}^{ji}f_{st}\overset{(-)}{R_{tu}^{ij}}.$$

The densities $\mathcal{D}^\xi$ and $\mathcal{D}^\eta$ were defined in Eqs. (52) and (54). Again all $\hat{f}$ are dressed only internally. All M and N quantities are defined similarly to the singlet case, e.g., $^R M_{\mu r} = -{}^R V_{kr}^Q(k\mu|Q)$.

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