Gauge-origin independent magneto-optical activity within coupled cluster response theory

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A gauge-origin invariant formulation of the frequency-dependent Verdet constant $V(\omega)$ of magneto-optical rotation and of the Faraday $\mathcal{B}$ term of magnetic circular dichroism for coupled-cluster wave functions is derived within the framework of variational response theory. Working expressions suitable for implementation in *ab initio* program packages are presented. These expressions have a structure similar to that of the expressions for the first hyperpolarizability and the two-photon transition moment, respectively, for the Verdet constant and the $\mathcal{B}$ term. The approach is general and can easily be extended to other similar frequency-dependent properties as well as to other wavefunction models. Pilot results at the CCSD level are presented for $V(\omega)$ of HF and H_2. © *2000 American Institute of Physics.* [S0021-9606(00)30233-1]

I. INTRODUCTION

The discovery of magneto-optical activity (MOA) dates back to 1845, when Faraday[1,2] observed that the application of a magnetic field in the direction of propagation of a plane polarized light beam passing through a piece of heavy glass affected the behavior of the beam. The effect consisted of a rotation (ϕ) of the plane of polarization of the ray induced by the longitudinal magnetic field; it was later found to occur in any sample and shown to be proportional to the magnetic field strength. The proportionality constant—which is frequency and temperature dependent—is known as the Verdet constant $V(\omega)$.[3] When the frequency approaches the absorption region of the sample, the light is attenuated and the rotation is accompanied by the development of an ellipticity (θ). Both aspects, rotation and ellipticity, are related to a differential behavior induced by the magnetic field of the right (R) and left (L) circularly polarized components of the plane polarized light beam. Traditionally, the rotation is associated with the anisotropy of the refractive indices $n_L - n_R$ and the ellipticity with the anisotropy of the absorption coefficients $n'_L - n'_R$. The latter effect is also called magnetic circular dichroism (MCD). Magneto-optical rotation (MOR) dispersion and MCD are also referred to as the ''Faraday effect.''

The fundamental equations relating the observed rotation and/or ellipticity to the microscopic properties of the sample have been derived in several equivalent ways. Buckingham and Stephens[4] used a conventional refractive-index approach, relating the complex rotation to the anisotropy of the complex refractive indices for the right and left circularly polarized components. The latter are expressed through the Maxwell equations in terms of averaged complex induced oscillating molecular moments, which are calculated quantum-mechanically. Focusing on the MCD, Stephens[5–7] rederived the equations for the ellipticity by means of semiclassical radiation absorption theory. Equivalent equations for the rotation and ellipticity have also been obtained by the refringent scattering approach, as shown for example by Barron.[8] Both the conventional refractive-index approach and the refringent-scattering approach have been successfully applied to several optical effects such as natural optical activity, linear birefringence, and Raman optical activity.

As for other optical properties, electron correlation is expected to play an important role in the *ab initio* calculation of the molecular properties characterizing the Faraday effect—that is, the Verdet constants and the Faraday $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{C}$ terms. In addition, the problem of the unphysical dependence on the origin of the vector potential (gauge-origin) for magnetic properties calculated with conventional finite basis sets needs to be addressed.

In the past, the calculation of molecular Verdet constants has appeared at various levels of *ab initio* theory (see, for example, Refs. 9–13). The Verdet constant has been calculated either from a spectral-representation expression,[13] or as combination of quadratic dipole–dipole–magnetic dipole response functions.[9–12] Using the Becquerel approximation,[14] which is exact only in the atomic case, propagators or linear response function expressions have also been used.[9,15] These calculations have mostly been limited to systems that are gauge-origin independent by symmetry; no general solution has so far been presented for a gauge-origin invariant calculation of Verdet constants. Indeed, in a recent paper, Pedersen *et al.* question the possibility of obtaining gauge-origin independent Verdet constants using a conventional coupled cluster ansatz for the wave function.[16]

Theoretical calculations of the Faraday terms of the MCD—in particular the $\mathcal{B}$ term—have mainly been per-

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formed by means of sum-over-states procedures. Recently, we presented an investigation of the MCD of two naturally gauge-invariant systems, reformulating the $\mathcal{B}$ term as a single residue of the dipole–dipole–magnetic dipole quadratic response function in a SCF and MCSCF parameterization.[17] A gauge-invariant method for calculating the $\mathcal{B}$ term was presented in the early 1970s by Seaman and Linderberg.[18] Self-consistent molecular orbitals at nonzero magnetic field were determined in the Pariser–Parr–Pople model, starting with an atomic orbital basis of London gauge including orbitals (LAOs or GIAOs),[19–21] and then employed to calculate transition moments according to the single-excited configuration-interaction and the random-phase approximations. The $\mathcal{B}$ term was then obtained by extrapolating to zero magnetic field the ratio between the field-dependent transition strength and the magnetic field strength—that is, essentially by numerical differentiation.

Inspired by Seaman and Linderberg's approach, we present here a gauge-origin invariant formulation of magneto-optical activity within the framework of coupled cluster (CC) response theory.[22–26] Our approach relies on the use of LAOs in connection with a reformulation of both the Verdet constant and the Faraday $\mathcal{B}$ term as total derivatives with respect to the strength of an external static magnetic field of, respectively, the dipole polarizability and dipole transition strength. For the latter properties, we employ the appropriate CC response expressions defined with respect to a SCF wave function optimized within the magnetic field. For the Verdet constant, this represents the first attempt to extend the London-orbital approach to the calculation of a frequency-dependent quadratic response property. To illustrate the validity of the proposed approach pilot results for the Verdet constant of HF at the CCSD level are finally presented. Also, the effect of using LAOs when calculating Verdet constants which are gauge-origin independent by symmetry is tested through preliminary calculations on H_2.

II. THE BASIC EQUATIONS

A. Conventional formulation

To treat MOR and MCD in a unified way, one may in analogy with Ref. 4 define the complex optical rotation $\tilde{\phi}$ per unit of path length

$$\tilde{\phi}=\phi+i\theta=\frac{\omega}{2c}\Delta\tilde{n}, \tag{1}$$

where $\Delta\tilde{n}=(n_L-n_R)+i(n'_L-n'_R)$ is the anisotropy of the complex refractive index. As shown for example in Refs. 4 and 8, the complex optical rotation for plane-polarized light traveling in the z direction of a space-fixed frame is related to the complex polarizability $\tilde{\alpha}_{\alpha\beta}$ (frequency argument implied),

$$\tilde{\phi}=\tfrac{1}{4}\omega\mu_0 cN[i\langle\tilde{\alpha}_{xy}-\tilde{\alpha}_{yx}\rangle], \tag{2}$$

where $\langle\cdots\rangle$ indicates an appropriate statistical average. In the nonabsorptive region, the complex polarizability $\tilde{\alpha}_{\alpha\beta}$ is defined as

$$\begin{aligned}\tilde{\alpha}_{\alpha\beta}&=\frac{2}{\hbar}\left\{\sum_{j\neq n}\frac{\omega_{jn}}{\omega_{jn}^2-\omega^2}\Re(\langle n|d_\alpha|j\rangle\langle j|d_\beta|n\rangle)\right.\\&\left.\quad+i\sum_{j\neq n}\frac{\omega}{\omega_{jn}^2-\omega^2}\Im(\langle n|d_\alpha|j\rangle\langle j|d_\beta|n\rangle)\right\}\\&=\alpha_{\alpha\beta}-i\alpha'_{\alpha\beta}=\tilde{\alpha}^*_{\beta\alpha},\end{aligned} \tag{3}$$

where d indicates the electric dipole moment operator and Eq. (2) reduces to

$$\phi=-\tfrac{1}{2}\omega\mu_0 cN\Im\langle\tilde{\alpha}_{xy}\rangle=\tfrac{1}{2}\omega\mu_0 cN\langle\alpha'_{xy}\rangle. \tag{4}$$

These definitions are readily generalized to the absorptive regions by introducing the line-shape functions f and g (see, for example, Ref. 8). For simplicity, we here restrict ourselves to the nonabsorptive region.

A linear dependence on the magnetic field is brought explicitly into Eq. (4) through the linear dependence of the antisymmetric polarizability α'_{xy} on the magnetic field and the orientational effect of the magnetic field on the permanent molecular magnetic moments. The polarizability $\alpha'_{\alpha\beta}$ is expanded in the magnetic field according to

$$\alpha'_{\alpha\beta}(B)=\alpha'_{\alpha\beta}(0)+\alpha'^{(m)}_{\alpha\beta,\gamma}B_\gamma+\mathcal{O}(B^2), \tag{5}$$

where B represents the magnetic field strength. Implicit summation over repeated indices is assumed here and throughout. The sum-over-states expression for the higher-order polarizability $\alpha'^{(m)}_{\alpha\beta,\gamma}$ is obtained from the definition of $\alpha'_{\alpha\beta}$ by substituting the magnetic field-dependent eigenstates j,n and their frequency separations $\omega_{jn}=\omega_j-\omega_n$ by the corresponding perturbational expansions in terms of zero-field eigenstates and frequency separations,[8,27]

$$\begin{aligned}\alpha'^{(m)}_{\alpha\beta,\gamma}&=-\frac{2}{\hbar^2}\sum_{j\neq n}\left\{\frac{2\omega\omega_{jn}}{(\omega_{jn}^2-\omega^2)^2}(m^j_\gamma-m^n_\gamma)\Im(\langle n|d_\alpha|j\rangle\langle j|d_\beta|n\rangle)+\frac{\omega}{(\omega_{jn}^2-\omega^2)}\Im\left[\sum_{k\neq n}\frac{\langle k|m_\gamma|j\rangle}{\omega_{kn}}\big(\langle n|d_\alpha|j\rangle\langle j|d_\beta|k\rangle\right.\right.\\&\left.\left.-\langle n|d_\beta|j\rangle\langle j|d_\alpha|k\rangle\big)+\sum_{k\neq j}\frac{\langle j|m_\gamma|k\rangle}{\omega_{kj}}\big(\langle n|d_\alpha|j\rangle\langle k|d_\beta|n\rangle-\langle n|d_\beta|j\rangle\langle k|d_\alpha|n\rangle\big)\right]\right\}\\&=-\frac{2}{\hbar}\sum_{j\neq n}\left\{\frac{2\omega\omega_{jn}}{\hbar(\omega_{jn}^2-\omega^2)^2}A'^{(jn)}_{\alpha\beta\gamma}+\frac{\omega}{(\omega_{jn}^2-\omega^2)}B'^{(jn)}_{\alpha\beta\gamma}\right\}.\end{aligned} \tag{6}$$

Here m_γ is a Cartesian component of the magnetic dipole operator and $m^k_\gamma=\langle k|m_\gamma|k\rangle$. The states n,j,k and the frequency separations ω_{kn}, ω_{kj}, ω_{jn} refer now to the unpertubed system ($B=0$). The orientational effect on the magnetic moment is

accounted for either by means of classical weighted Boltzmann average with the potential energy $U=-m^n_\gamma B_\gamma$ or by means of an unweighted quantum statistical average.[8] For a fluid sample, the resulting rotation with respect to the molecular frame becomes

$$\phi=\frac{1}{12}\omega\mu_0 cNB_z\epsilon_{\alpha\beta\gamma}\left(\alpha'^{(m)}_{\alpha\beta,\gamma}+\frac{1}{kT}m^n_\gamma\alpha'_{\alpha\beta}\right)=V(\omega)B_z, \tag{7}$$

where we have introduced the Verdet constant $V(\omega)=\phi/B_z$. The symbol $\epsilon_{\alpha\beta\gamma}$ was used for the Levi–Civita tensor. Note that, if n is the ground state, the second term in parentheses is zero for closed-shell systems as the magnetic dipole is quenched. An analogous expansion for $\tilde{\alpha}_{\alpha\beta}$ followed by orientational averaging leads to a similar equation for the generalized complex rotation Eq. (2).

The (averaged) Faraday $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{C}$ terms, used to rationalize the MCD, are easily identified from the tensors so far introduced by splitting the total rotation (or more rigorously the complex rotation) into contributions from a particular ''transition'' $n\rightarrow j$—that is, $\phi=\Sigma_{j\neq n}\phi(n\rightarrow j)$. According to the current convention,[8,28]

$$\phi(n\rightarrow j)=-\frac{\mu_0 cNB_z}{3\hbar}\left\{\frac{2\omega^2\omega_{jn}}{\hbar(\omega^2_{jn}-\omega^2)^2}\mathcal{A}(n\rightarrow j)+\frac{\omega^2}{\omega^2_{jn}-\omega^2}\left[\mathcal{B}(n\rightarrow j)+\frac{1}{kT}\mathcal{C}(n\rightarrow j)\right]\right\}, \tag{8}$$

$$\mathcal{A}(n\rightarrow j)=\tfrac{1}{6}\epsilon_{\alpha\beta\gamma}(3A'^{(jn)}_{\alpha\beta\gamma})=\tfrac{1}{2}\epsilon_{\alpha\beta\gamma}(m^j_\gamma-m^n_\gamma)\Im(\langle n|d_\alpha|j\rangle\langle j|d_\beta|n\rangle), \tag{9}$$

$$\mathcal{B}(n\rightarrow j)=\tfrac{1}{6}\epsilon_{\alpha\beta\gamma}(3B'^{(jn)}_{\alpha\beta\gamma})=\epsilon_{\alpha\beta\gamma}\Im\left[\sum_{k\neq n}\frac{\langle k|m_\gamma|n\rangle}{\hbar\omega_{kn}}\langle n|d_\alpha|j\rangle\langle j|d_\beta|k\rangle+\sum_{k\neq j}\frac{\langle j|m_\gamma|k\rangle}{\hbar\omega_{kj}}\langle n|d_\alpha|j\rangle\langle k|d_\beta|n\rangle\right], \tag{10}$$

$$\mathcal{C}(n\rightarrow j)=\tfrac{1}{2}\epsilon_{\alpha\beta\gamma}m^n_\gamma\Im(\langle n|d_\alpha|j\rangle\langle j|d_\beta|n\rangle). \tag{11}$$

For molecules with a nondegenerate ground state n and a nondegenerate state j only the $\mathcal{B}$ term is nonvanishing. In the following, we are concerned with the calculation of $\mathcal{B}(n\rightarrow j)$ and of the Verdet constant $V(\omega)$.

B. Derivative formulation

The Verdet constant and the Faraday $\mathcal{B}$ term may alternatively be expressed as derivatives of property expressions with respect to the magnetic induction. Expanding the rotation in the field according to[29]

$$\langle\phi\rangle_B=\langle\phi\rangle+B_z\left\{\left\langle\left(\frac{d\phi}{dB_z}\right)_0\right\rangle+\frac{1}{kT}(\langle\phi m^n_z\rangle+\langle\phi\rangle\langle m^n_z\rangle)\right\}+\mathcal{O}(B^2)=B_z\left\{\left\langle\left(\frac{d\phi}{dB_z}\right)_0\right\rangle+\frac{1}{kT}\langle\phi m^n_z\rangle\right\}+\mathcal{O}(B^2), \tag{12}$$

where the averages on the r.h.s. are taken at zero magnetic field, we can immediately relate the Verdet constant for a closed-shell system to the derivative of the frequency-dependent antisymmetric polarizability (i.e., the imaginary part of the complex polarizability),

$$V(\omega)=\left\langle\left(\frac{d\phi}{dB_z}\right)_0\right\rangle=\frac{1}{12}\omega\mu_0 cN\epsilon_{\alpha\beta\gamma}\left(\frac{d\alpha'_{\alpha\beta}(-\omega;\omega)}{dB_\gamma}\right)_0=-\frac{1}{12}\omega\mu_0 cN\epsilon_{\alpha\beta\gamma}\Im\left(\frac{d\tilde{\alpha}_{\alpha\beta}(-\omega;\omega)}{dB_\gamma}\right)_0 \tag{13}$$

and identify the Faraday $\mathcal{B}(n\rightarrow j)$ term of a closed-shell system without degenerate states from the derivative of a one-photon transition strength

$$\mathcal{B}(n\rightarrow j)=\frac{1}{2}\epsilon_{\alpha\beta\gamma}\left(\frac{d\Im(\langle n|d_\alpha|j\rangle\langle j|d_\beta|n\rangle)}{dB_\gamma}\right)_0=\frac{1}{2}\epsilon_{\alpha\beta\gamma}\Im\left(\frac{dS^{\alpha\beta}_{nj}}{dB_\gamma}\right)_0. \tag{14}$$

The derivative formulation is advantageous for several reasons. First, contrary to the conventional sum-over-states representation, it does not require that all excited states are explicitly calculated. Rather, one can simply identify the property expressions to be differentiated in terms of linear response functions and corresponding residues, and then differentiate these response function expressions for a given wave function approximation to obtain the Verdet constant and the Faraday $\mathcal{B}$ term. Second, we also demonstrate that, with London atomic orbitals and using response function expressions where the orbitals are allowed to relax in the magnetic field, $V(\omega)$ and $\mathcal{B}$ may be obtained gauge-origin independent without consideration whether the Ehrenfest theorem is satisfied for one-electron operators in the chosen wavefunction approximation. Difficulties in ensuring gauge-origin independence are encountered if $V(\omega)$ and $\mathcal{B}$ are calculated in terms of quadratic response functions and residues of quadratic response functions.[10]

III. GAUGE-ORIGIN INVARIANT MOA WITHIN CC RESPONSE THEORY

As physical observables, the Verdet constant $V(\omega)$ and the Faraday $\mathcal{B}$ term must be independent of the choice of the gauge origin. In approximate calculations, however, gauge-origin independence is not necessarily satisfied. In the next subsections, we describe in detail how gauge-origin independent expressions for $V(\omega)$ and $\mathcal{B}$ can be obtained from the previous derivative formulation of the response properties and the use of London orbitals. We restrict ourselves to the CC model but emphasize that the same strategy may be applied for other approximate wave function models.

First we summarize how the polarizability and oscillator strength can be calculated in CC response theory. We then discuss the use of LAOs to parametrize the magnetic field dependence in the polarizability and oscillator strength. In

particular, we demonstrate that the magnetic-field orbital-relaxed property expressions to be differentiated are independent of the chosen connection scheme and identical to that obtained using the symmetric connection. As the molecular orbital integrals in the symmetric connection[30] are independent of the gauge origin, we obtain a gauge-invariant Verdet constant and $\mathcal{B}$ term.

A. The ansatz

In CC response theory, the frequency-dependent dipole polarizability and the dipole oscillator strengths can be formulated as derivatives with respect to the (frequency-dependent) electric-field strengths of the real part of the time-averaged quasienergy Lagrangian[26,31] and the time-averaged transition moment Lagrangians,[32] both of which are generalizations of the energy Lagrangian introduced for the treatment of time-independent properties.[33] To obtain these derivatives, a time-dependent CC state is used in which the orbitals are not allowed to relax with respect to the electric perturbation.[26,31,32] The time-dependent Hamiltonian employed can be written as

$$\begin{aligned} H(t,E) &= H + V(t,E) \\ &= H - d_\gamma [E_\gamma(\omega_\gamma)\exp(-i\omega_\gamma t) \\ &\quad + E_\gamma(-\omega_\gamma)\exp(i\omega_\gamma t)] \quad (\gamma = x,y,z), \end{aligned} \tag{15}$$

where H is the Hamiltonian for the unperturbed system, $E(\omega)$ the electric field strength, and d the static electric dipole moment operator.

The resulting expressions for the electric-field-unrelaxed frequency dependent polarizability[26,31] and for the one-photon transition strength[26,32] are

$$\begin{aligned} \alpha_{\alpha\beta}(\omega_\alpha,\omega_\beta) = -\tfrac{1}{2}\hat{C}^{\pm\omega}\{ &\eta^{d_\alpha} t^{d_\beta}(\omega_\beta) + \boldsymbol{F} t^{d_\alpha}(\omega_\alpha) t^{d_\beta}(\omega_\beta) \\ &+ \eta^{d_\beta} t^{d_\alpha}(\omega_\alpha)\} \end{aligned} \tag{16}$$

with $\omega_\alpha = -\omega_\beta = \omega$, and

$$S^{\alpha\beta}_{nj} = \tfrac{1}{2}\{M^{d_\alpha}_{n\leftarrow j} M^{d_\beta}_{j\leftarrow n} + (M^{d_\beta}_{n\leftarrow j} M^{d_\alpha}_{j\leftarrow n})^*\}, \tag{17}$$

where the left and right one-photon dipole transition moments $M^d_{n\leftarrow j}$ and $M^d_{j\leftarrow n}$ are given by[26,32]

$$M^d_{n\leftarrow j} = \overline{\xi^d}(-\omega_j) E^j(\omega_j) = \eta^d E^j(\omega_j) + \overline{M^j}(\omega_j)\xi^d, \tag{18}$$

$$M^d_{j\leftarrow n} = \overline{E^j}(-\omega_j)\xi^d. \tag{19}$$

The operator $\hat{C}^{\pm\omega}$ enforces time-reversal symmetry on the CC polarizability by symmetrizing with respect to simultaneous complex conjugation and inversion of the sign of the frequency. The vector-matrix notation of Refs. 26 and 32 was used. The various matrices and vectors are defined as[26,31,32]

$$\xi^d_\mu = \langle \overline{\mu}|d|\mathrm{CC}\rangle, \tag{20}$$

$$\eta^d_\mu = \langle \Lambda|[d,\tau_\mu]|\mathrm{CC}\rangle, \tag{21}$$

$$F_{\mu\nu} = \langle \Lambda|[[H,\tau_\mu],\tau_\nu]|\mathrm{CC}\rangle, \tag{22}$$

and

$$\overline{\xi^d}(\omega_d) = \eta^d + \boldsymbol{F} t^d(\omega_d), \tag{23}$$

where

$$|\mathrm{CC}\rangle = \exp(T)|\mathrm{HF}\rangle, \tag{24}$$

$$\langle \overline{\mu}| = \langle \mathrm{HF}|\tau^\dagger_\mu \exp(-T) = \langle \mu|\exp(-T), \tag{25}$$

$$\langle \Lambda| = \langle \mathrm{HF}|\left(1 + \sum_\mu \overline{t}_\mu \tau^\dagger_\mu\right)\exp(-T). \tag{26}$$

The cluster operator is given by $T = \Sigma_\mu t_\mu \tau_\mu$, with τ_μ an excitation operator and t_μ the associated amplitude (for each excitation level μ). To zero order with respect to the time-dependent electric-field perturbation, the amplitudes t are obtained from the CC equations,

$$\langle \mu|\exp(-T) H \exp(T)|\mathrm{HF}\rangle = 0. \tag{27}$$

The zero-order Lagrange multipliers $\overline{t}$ are the solutions of the set of linear equations

$$\eta + \overline{t}\boldsymbol{A} = 0, \tag{28}$$

where

$$\eta_\mu = \langle \mathrm{HF}|[H,\tau_\mu]|\mathrm{CC}\rangle, \tag{29}$$

and the CC Jacobian $\boldsymbol{A}$ is given by

$$A_{\mu\nu} = \langle \overline{\mu}|[H,\tau_\nu]|\mathrm{CC}\rangle. \tag{30}$$

The left and right excitation vectors $\overline{E^j}(-\omega_j)$ and $E^j(\omega_j)$ are the solutions of the linear equations

$$\overline{E^j}\boldsymbol{A} = \omega_j \overline{E^j}, \quad \boldsymbol{A}E^j = \omega_j E^j \tag{31}$$

under the biorthonormality condition $\overline{E^j}E^f = \delta_{jf}$. The frequency argument in $\overline{E^j}$ and E^j is conventional.[32,34] The first-order responses $t^d(\omega_d)$ of the amplitudes to the electric field are obtained from the equations

$$\xi^d + [\boldsymbol{A} - \omega_d \boldsymbol{1}] t^d(\omega_d) = 0. \tag{32}$$

The intermediate vector $\overline{M^j}(\omega_j)$ is found by solving[32]

$$\overline{M^j}(\omega_j)(\boldsymbol{A} + \omega_j \boldsymbol{1}) = -\boldsymbol{F}E^j(\omega_j). \tag{33}$$

In second quantization, the dipole and Hamiltonian operators are expressed as

$$d = \sum_{pq} d_{pq} E_{pq}, \tag{34}$$

$$H = \sum_{pq} h_{pq} E_{pq} + \frac{1}{2}\sum_{pqrs} g_{pqrs} e_{pqrs}, \tag{35}$$

where $E_{pq} = \Sigma_{\sigma=\alpha,\beta} a^\dagger_{p\sigma} a_{q\sigma}$, $e_{pqrs} = E_{pq}E_{rs} - \delta_{qr}E_{ps}$, and d_{pq}, h_{pq} and g_{pqrs} are the one- and two-electron integrals over the orthonormal basis of molecular orbitals.

B. The introduction of the magnetic field

In the presence of an external *static* magnetic field, the polarizability and the oscillator strength may be obtained in a two-step approach, replacing the unperturbed Hamiltonian in Eq. (15) by the Hamiltonian for the system in presence of the static magnetic field

$$H(\boldsymbol{B}) = H - m_{O,\gamma}B_\gamma - \tfrac{1}{2}\xi_{O,\gamma\delta}B_\gamma B_\delta \quad (\gamma,\delta = x,y,z) \tag{36}$$

and treating all states as magnetic-field dependent. The time-dependent Schrödinger equation for the interaction between the polarized light and the system is thus solved for a static Hamiltonian that contains the interaction with the magnetic field.

In the Hamiltonian, both the magnetic dipole moment operator m_O and the diamagnetic magnetizability operator ξ_O refer to an arbitrarily chosen gauge origin $\boldsymbol{O}$. Alternatively, the Hamiltonian $H(\boldsymbol{B})$ can be written in terms of the vector potentials of the electrons with respect to the gauge origin $\boldsymbol{A}_i \equiv \boldsymbol{A}(\boldsymbol{r}_{iO}) = \frac{1}{2}\boldsymbol{B}\times(\boldsymbol{r}_i - \boldsymbol{O})$ as

$$H(\boldsymbol{A}) = \frac{1}{2}\sum_i \, (-i\nabla_i + \boldsymbol{A}_i)^2 - \sum_{i,K} \frac{Z_K}{r_{iK}} + \frac{1}{2}\sum_{i\neq j} \frac{1}{r_{ij}}. \quad (37)$$

The dependence of the Hamiltonian $H(\boldsymbol{B})$ on an arbitrarily chosen gauge origin is a manifestation of the gauge-origin problem, which hampers the calculation of magnetic molecular properties within approximate methods.

Thus, in the presence of a magnetic field, the polarizability and the oscillator strength are still defined according to Eqs. (16)–(33), where all contributions become magnetic-field dependent, for example, the Jacobian matrix becomes

$$\boldsymbol{A}_{\mu\nu}(\boldsymbol{B}) = \langle \overline{\mu}(\boldsymbol{B}) | [H(\boldsymbol{B}), \tau_\nu(\boldsymbol{B})] | \mathrm{CC}(\boldsymbol{B}) \rangle, \quad (38)$$

where $|\mathrm{CC}(\boldsymbol{B})\rangle = \exp T(\boldsymbol{B}) |\mathrm{HF}(\boldsymbol{B})\rangle$ and analogously for $\langle \overline{\mu}(\boldsymbol{B})|$.

In terms of an orthonormal set of field-dependent orbitals, the second-quantization form of the Hamiltonian $H(\boldsymbol{B})$ becomes[30,35]

$$H(\boldsymbol{A}) = \sum_{pq} \, h_{pq}(\boldsymbol{A}) E_{pq}(\boldsymbol{A}) + \frac{1}{2}\sum_{pqrs} \, g_{pqrs}(\boldsymbol{A}) e_{pqrs}(\boldsymbol{A}), \quad (39)$$

where the field dependence in the one-electron part arises from the implicit field dependence in the orbitals and the creation/annihilation operators as well as from the explicit dependence in the one-electron operator itself. Note that, in the second quantization formalism, also the dipole moment operator becomes magnetic field dependent, through the implicit dependence in the magnetic field of the orbitals and of the creation/annihilation operators.

C. The London orbitals and the relationship between different connections

Suppose that we have performed a Hartree–Fock calculation at zero magnetic field and obtained the wave function $|\mathrm{HF}\rangle$ and a set of optimized orbitals

$$\psi_p(0) = \sum_\mu \, \chi_\mu C^{(0)}_{\mu p}, \quad (40)$$

where χ_μ is a conventional Gaussian orbital centered on nucleus M at position $\boldsymbol{R}_M$. For any given magnetic induction $\boldsymbol{B}$, a basis of atomic field-dependent orbitals, the London orbitals,[19] $\{\varphi_\mu\}$ can be defined according to

$$\varphi_\mu(\boldsymbol{B}) = \exp(-i\boldsymbol{A}^e_{MO}\cdot\boldsymbol{r})\chi_\mu, \quad (41)$$

where $\boldsymbol{A}^e_{MO}$ is the vector potential at the position $\boldsymbol{R}_{MO} = \boldsymbol{R}_M - \boldsymbol{O}$ of the nucleus M with respect to the chosen gauge origin,

$$\boldsymbol{A}^e_{\mathrm{MO}} = \tfrac{1}{2}\boldsymbol{B}\times\boldsymbol{R}_{MO}, \quad (42)$$

and $\boldsymbol{r}$ is the electron coordinate. Note that in absence of the perturbation $\varphi_\mu(0) = \chi_\mu$.

The LAOs can be employed to define an orthonormalized basis of molecular field-dependent orbitals, from which an Hamiltonian operator defined at all values of the field can be constructed. This may be accomplished in two steps. First, from the LAOs and the MO coefficients $C^{(0)}_{\mu n}$ of the optimized orbitals at zero magnetic field, the *unmodified molecular orbitals* (UMOs) are constructed as[30]

$$\phi_q(\boldsymbol{B}) = \sum_\mu \, \varphi_\mu(\boldsymbol{B}) C^{(0)}_{\mu q}. \quad (43)$$

Second, assuming that their overlap matrix $\boldsymbol{S}$ is nonsingular, the UMOs are further transformed into a set of *orthonormalized molecular orbitals* (OMOs),[30]

$$\psi_p(\boldsymbol{B}) = \sum_q \, \phi_q(\boldsymbol{B}) R_{qp}(\boldsymbol{B}). \quad (44)$$

The transformation matrix $\boldsymbol{R} = \boldsymbol{S}^{-1/2}\boldsymbol{U}$, where $\boldsymbol{U}$ is unitary defines the different *connection schemes*[36,37] which establish a one-to-one correspondence between orbitals at different values of the field. If $\boldsymbol{U} = \boldsymbol{1}$, the OMO basis in Eq. (44) corresponds to a symmetric orthogonalization of the UMO basis—the *symmetric connection*.[30] For any general connection scheme,

$$\psi^{\mathrm{g}}_p = \sum_r \, \psi^{\mathrm{s}}_r U^{\mathrm{g}}_{rp} = \sum_r \, \psi^{\mathrm{s}}_r [e^{-x^{\mathrm{g}}}]_{rp}, \quad (45)$$

where the unitary matrix $\boldsymbol{U}^{\mathrm{g}}$ was expressed in terms of an anti-Hermitian matrix $\boldsymbol{x}^{\mathrm{g}}$. The indices ''g'' and ''s'' are used to distinguish between a general connection and the symmetric connection and explicit reference to the field dependence is suppressed for ease of notation. The orbital indices p, q, r, s are used for unspecified (occupied or virtual) orbitals, i, j, k, l for occupied, and a, b, c, d for virtual. Note that the OMOs are not the optimized orbitals in the presence of the external perturbation but that they become identical to the optimized orbitals for the unperturbed system in absence of the perturbation.

D. The (effective) relaxed Hamiltonian and dipole operator

We now consider a general connection OMO basis and employ it to expand the Hamiltonian and parametrize the optimized Hartree–Fock state in the presence of the field according to (neglecting the purely nuclear contributions)

$$H(\boldsymbol{B}) = \sum_{pq} \, h^{\mathrm{g}}_{pq} E^{\mathrm{g}}_{pq} + \frac{1}{2}\sum_{pqrs} \, g^{\mathrm{g}}_{pqrs} e^{\mathrm{g}}_{pqrs}, \quad (46)$$

$$|\mathrm{HF}(\boldsymbol{B})\rangle = \exp(-\tilde{\kappa}_{\mathrm{g}})|\mathrm{HF}_{\mathrm{g}}\rangle, \quad (47)$$

where $|\mathrm{HF_g}\rangle$ is a determinantal wave function built from the creation operators for the general OMO basis, and the operator

$$\tilde{\kappa}_\mathrm{g} = \sum_{pq}^{\text{nonred.}} \tilde{\kappa}^\mathrm{g}_{pq} E^\mathrm{g}_{pq} \tag{48}$$

generates (nonredundant) orbital rotations among the OMOs. Note that E^g_{pq}, $|\mathrm{HF_g}\rangle$, and $\tilde{\kappa}^\mathrm{g}_{pq}$ are magnetic field-dependent, but their dependence is suppressed for ease of notation.

To obtain $V(\omega)$ and $\mathcal{B}$ we need to take the total derivative of matrix elements such as Eq. (38), that is, the derivative of generalized transition expectation values between states defined at the same value of the field. As a consequence of Wick's theorem, we can then neglect the magnetic field (and gauge) dependence of the elementary creation/annihilation operators corresponding to the OMO basis.[30,33] As discussed in Ref. 37, this may be viewed as expanding the elementary operators at a given value of the field in the elementary operators at zero field. The Hamiltonian in Eq. (46) and the field-dependent Hartree–Fock state in Eq. (47) can then be written in the ''effective'' form,

$$H(\boldsymbol{B}) = H_\mathrm{g} = \sum_{pq} h^\mathrm{g}_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} g^\mathrm{g}_{pqrs} e_{pqrs}, \tag{49}$$

$$|\mathrm{HF}(\boldsymbol{B})\rangle = \exp(-\kappa_\mathrm{g})|\mathrm{HF}\rangle, \tag{50}$$

where E_{pq}, e_{pqrs}, and $|\mathrm{HF}\rangle$ refer to the optimized basis in absence of the perturbation, and

$$\kappa_\mathrm{g} = \sum_{pq}^{\text{nonred.}} \kappa^\mathrm{g}_{pq} E_{pq}. \tag{51}$$

The elements κ^g_{pq} of the anti-Hermitian matrix $\boldsymbol{\kappa}^\mathrm{g}$, which depend implicitly on the field, are nonzero only for the occupied-virtual and virtual-occupied blocks—that is, they are the *nonredundant* parameters as determined from the (effective) Hartree–Fock orbital optimization condition,

$$\begin{aligned}&\langle \mathrm{HF}(\boldsymbol{B})|[E_{pq}(\boldsymbol{B}), H(\boldsymbol{B})]|\mathrm{HF}(\boldsymbol{B})\rangle = 0 \\ &\quad \rightarrow \langle \mathrm{HF_g}|\exp(\kappa_\mathrm{g})[\exp(-\kappa_\mathrm{g}) E_{pq} \exp(\kappa_\mathrm{g}), H_\mathrm{g}] \\ &\qquad \times \exp(-\kappa_\mathrm{g})|\mathrm{HF_g}\rangle = \langle \mathrm{HF}|[E_{pq}, H^\kappa_\mathrm{g}]|\mathrm{HF}\rangle = 0,\end{aligned} \tag{52}$$

where we have introduced the (effective) *relaxed Hamiltonian* in the given general-connection OMO basis

$$H^\kappa_\mathrm{g} = \exp(\kappa_\mathrm{g}) H_\mathrm{g} \exp(-\kappa_\mathrm{g}). \tag{53}$$

In the following, we shall consider the structure of this operator.

Inserting Eq. (45) into the definition of the integrals of H_g and introducing the anti-Hermitian operator,

$$x_\mathrm{g} = \sum_{pq} x^\mathrm{g}_{pq} E_{pq}, \tag{54}$$

where x^g_{pq} are the elements of the anti-Hermitian matrix $\boldsymbol{x}^\mathrm{g}$, the Hamiltonian H_g may be written as

$$H_\mathrm{g} = \exp(x_\mathrm{g}) H_\mathrm{s} \exp(-x_\mathrm{g}), \tag{55}$$

where

$$H_\mathrm{s} = \sum_{pq} h^\mathrm{s}_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} g^\mathrm{s}_{pqrs} e_{pqrs} \tag{56}$$

is the effective Hamiltonian in the symmetric connection. With this reformulation of H_g, the relaxed Hamiltonian in the given general-connection OMO basis becomes

$$\begin{aligned}H^\kappa_\mathrm{g} &= \exp(\kappa_\mathrm{g})\exp(x_\mathrm{g}) H_\mathrm{s} \exp(-x_\mathrm{g})\exp(-\kappa_\mathrm{g}) \\ &= \exp(\kappa_\mathrm{rd})\exp(\kappa_\mathrm{s}) H_\mathrm{s} \exp(-\kappa_\mathrm{s})\exp(-\kappa_\mathrm{rd}) \\ &\equiv \exp(\kappa_\mathrm{rd}) H^\kappa_\mathrm{s} \exp(-\kappa_\mathrm{rd}),\end{aligned} \tag{57}$$

where

$$\kappa_\mathrm{s} = \sum_{pq}^{\text{nonred.}} \kappa^\mathrm{s}_{pq} E_{pq}, \tag{58}$$

$$\kappa_\mathrm{rd} = \sum_{ij}^{\text{occ}} \kappa^\mathrm{rd}_{ij} E_{ij} + \sum_{ab}^{\text{vir}} \kappa^\mathrm{rd}_{ab} E_{ab}, \tag{59}$$

with the anti-Hermitian matrices $\boldsymbol{\kappa}^\mathrm{s}$ and $\boldsymbol{\kappa}^\mathrm{rd}$ having nonzero elements corresponding to the nonredundant and redundant orbital rotations, respectively. The equivalence of the second and third expressions in Eq. (57) follows since these expressions represent two equivalent parameterizations of a general unitary matrix.[38]

Let us derive a set of equations for the nonredundant parameters $\boldsymbol{\kappa}^\mathrm{s}$. Inserting Eq. (57) in Eq. (52), we obtain

$$\begin{aligned}&\langle \mathrm{HF}|[E_{pq}, \exp(\kappa_\mathrm{rd}) H^\kappa_\mathrm{s} \exp(-\kappa_\mathrm{rd})]|\mathrm{HF}\rangle \\ &\quad = \langle \mathrm{HF}|\exp(\kappa_\mathrm{rd})[\exp(-\kappa_\mathrm{rd}) E_{pq} \exp(\kappa_\mathrm{rd}), H^\kappa_\mathrm{s}] \\ &\qquad \times \exp(-\kappa_\mathrm{rd})|\mathrm{HF}\rangle = 0,\end{aligned} \tag{60}$$

where pq refers to the nonredundant parameters ($pq = ai$, ia). Because of the relations

$$\exp(-\kappa_\mathrm{rd})|\mathrm{HF}\rangle = |\mathrm{HF}\rangle, \tag{61}$$

$$\exp(-\kappa_\mathrm{rd}) E_{pq} \exp(\kappa_\mathrm{rd}) = \sum_{rs}^{\text{nonred.}} C_{rs} E_{rs} \tag{62}$$

we find that Eq. (52) [or equivalently Eq. (60)] is satisfied if

$$\langle \mathrm{HF}|[E_{rs}, \exp(-\kappa_\mathrm{s}) H_\mathrm{s} \exp(\kappa_\mathrm{s})]|\mathrm{HF}\rangle = 0. \tag{63}$$

This corresponds to the effective Hartree–Fock optimization condition in the symmetric connection, from which the nonredundant parameters, and thus the effective relaxed H^κ_s operator, are determined.

The redundant parameters $\boldsymbol{\kappa}^\mathrm{rd}$ of Eq. (57) are not determined by the orbital optimization condition, but are implicitly given through the choice of κ_g, x_g, and κ_s. Since the relaxed Hamiltonian H^κ_g is later used only in contexts where the property considered is invariant to redundant orbital rotations, explicit knowledge of these parameters is therefore not required.

Thus, even though the parameters $\boldsymbol{\kappa}^\mathrm{g}$ and $\boldsymbol{\kappa}^\mathrm{s}$ determined by Eq. (52) and Eq. (63), respectively, are not the same, *the final effective relaxed Hamiltonian in the general connection is for all practical purposes* (i.e., *to within a redundant orbital transformation*) *equivalent to the effective relaxed Hamiltonian in the symmetric connection*. This is an impor-

tant result also in the sense that the symmetric connection may not always be the most useful approach from a numerical point of view.[39] Similar relations may be derived for other operators. In particular, for the effective *relaxed dipole moment operator*, we obtain

$$\begin{aligned} d_{\mathrm{g}}^{\kappa} &= \exp(\kappa_{\mathrm{g}}) d_{\mathrm{g}} \exp(-\kappa_{\mathrm{g}}) \\ &= \exp(\kappa_{\mathrm{g}}) \exp(x_{\mathrm{g}}) d_{\mathrm{s}} \exp(-x_{\mathrm{g}}) \exp(-\kappa_{\mathrm{g}}) \\ &= \exp(\kappa_{\mathrm{rd}}) \exp(\kappa_{\mathrm{s}}) d_{\mathrm{s}} \exp(-\kappa_{\mathrm{s}}) \exp(-\kappa_{\mathrm{rd}}) \\ &\equiv \exp(\kappa_{\mathrm{rd}}) d_{\mathrm{s}}^{\kappa} \exp(-\kappa_{\mathrm{rd}}), \end{aligned} \tag{64}$$

with $d_{\mathrm{g}} = \Sigma_{pq} d_{pq}^{\mathrm{g}} E_{pq}$ and $d_{\mathrm{s}} = \Sigma_{pq} d_{pq}^{\mathrm{s}} E_{pq}$.

E. The effective CC equations and matrix elements

In the presence of the magnetic field, the CC wave function is parametrized in the OMO basis as

$$|\mathrm{CC}(\mathbf{B})\rangle = \exp(-\tilde{\kappa}_{\mathrm{g}}) \exp(\tilde{T}_{\mathrm{g}}) |\mathrm{HF}_{\mathrm{g}}\rangle, \tag{65}$$

where $\tilde{T}_{\mathrm{g}} = \Sigma_{\mu} \tilde{t}_{\mu}^{\mathrm{g}} \tau_{\mu}^{\mathrm{g}}$. Analogously,

$$\begin{aligned} \langle \overline{\tilde{\mu}}(\mathbf{B})| &= \langle \mathrm{HF}_{\mathrm{g}}| \tau_{\mu}^{\mathrm{g}\dagger} \exp(-\tilde{T}_{\mathrm{g}}) \exp(\tilde{\kappa}_{\mathrm{g}}) \\ &= \langle \mu_{\mathrm{g}}| \exp(-\tilde{T}_{\mathrm{g}}) \exp(\tilde{\kappa}_{\mathrm{g}}), \end{aligned} \tag{66}$$

$$\langle \Lambda(\mathbf{B})| = \langle \mathrm{HF}_{\mathrm{g}}| \left(1 + \sum_{\mu} \tilde{\bar{t}}_{\mu}^{\mathrm{g}} \tau_{\mu}^{\mathrm{g}\dagger} \right) |\exp(-\tilde{T}_{\mathrm{g}}) \exp(\tilde{\kappa}_{\mathrm{g}}). \tag{67}$$

Again, according to Wick's theorem, we can expand our creation/annihilation OMO basis in the generator basis at the expansion point, only retaining an implicit dependence on the magnetic field in the orbital and wavefunction parameters,

$$|\mathrm{CC}(\mathbf{B})\rangle = \exp(-\kappa_{\mathrm{g}}) \exp(T_{\mathrm{g}}) |\mathrm{HF}\rangle, \tag{68}$$

$$\begin{aligned} \langle \overline{\mu}(\mathbf{B})| &= \langle \mathrm{HF}| \tau_{\mu}^{\dagger} \exp(-T_{\mathrm{g}}) \exp(\kappa_{\mathrm{g}}) \\ &= \langle \mu| \exp(-T_{\mathrm{g}}) \exp(\kappa_{\mathrm{g}}), \end{aligned} \tag{69}$$

$$\langle \Lambda(\mathbf{B})| = \langle \mathrm{HF}| \left(1 + \sum_{\mu} \overline{t}_{\mu}^{\mathrm{g}} \tau_{\mu}^{\dagger} \right) |\exp(-T_{\mathrm{g}}) \exp(\kappa_{\mathrm{g}}), \tag{70}$$

where $T_{\mathrm{g}} = \Sigma_{\mu} t_{\mu}^{\mathrm{g}} \tau_{\mu}$.

The CC amplitudes are obtained by solving the (effective) *relaxed CC equations*,

$$\langle \mu| \exp(-T_{\mathrm{g}}) H_{\mathrm{g}}^{\kappa} \exp(T_{\mathrm{g}}) |\mathrm{HF}\rangle = 0. \tag{71}$$

Introducing the relation between the operators in general and symmetric connection, Eq. (57), we get

$$\begin{aligned} &\langle \mu| \exp(-T_{\mathrm{g}}) H_{\mathrm{g}}^{\kappa} \exp(T_{\mathrm{g}}) |\mathrm{HF}\rangle \\ &\quad = \langle \mu| \exp(-T_{\mathrm{g}}) \exp(\kappa_{\mathrm{rd}}) H_{\mathrm{s}}^{\kappa} \exp(-\kappa_{\mathrm{rd}}) \exp(T_{\mathrm{g}}) |\mathrm{HF}\rangle \\ &\quad = 0 \equiv \langle \mu| \exp(\kappa_{\mathrm{rd}}) \exp(-T') H_{\mathrm{s}}^{\kappa} \exp(T') |\mathrm{HF}\rangle = 0, \end{aligned} \tag{72}$$

and the *effective* expressions for the vectors and matrix elements (for the general connection) to be differentiated become

$$\begin{aligned} \xi_{\mu}^{d} &= \langle \mu| \exp(-T_{\mathrm{g}}) d_{\mathrm{g}}^{\kappa} \exp(T_{\mathrm{g}}) |\mathrm{HF}\rangle \\ &= \langle \mu| \exp(-T_{\mathrm{g}}) \exp(\kappa_{\mathrm{rd}}) d_{\mathrm{s}}^{\kappa} \exp(-\kappa_{\mathrm{rd}}) \exp(T_{\mathrm{g}}) |\mathrm{HF}\rangle \\ &= \langle \mu| \exp(\kappa_{\mathrm{rd}}) \exp(-T') d_{\mathrm{s}}^{\kappa} \exp(T') |\mathrm{HF}\rangle, \end{aligned} \tag{73}$$

$$\begin{aligned} \eta_{\mu}^{d} &= \langle \mathrm{HF}| \left(1 + \sum_{\lambda} \overline{t}_{\lambda}^{\mathrm{g}} \tau_{\lambda}^{\dagger} \right) \exp(-T_{\mathrm{g}}) [d_{\mathrm{g}}^{\kappa}, \tau_{\mu}] \exp(T_{\mathrm{g}}) |\mathrm{HF}\rangle \\ &= \langle \mathrm{HF}| \left(1 + \sum_{\lambda} \overline{t}_{\lambda}^{\mathrm{g}} \tau_{\lambda}^{\dagger} \right) \exp(-T_{\mathrm{g}}) \\ &\quad \times [\exp(\kappa_{\mathrm{rd}}) d_{\mathrm{s}}^{\kappa} \exp(-\kappa_{\mathrm{rd}}), \tau_{\mu}] \exp(T_{\mathrm{g}}) |\mathrm{HF}\rangle \\ &= \langle \mathrm{HF}| \left(1 + \sum_{\lambda} \overline{t}_{\lambda}^{\mathrm{g}} \tau_{\lambda}^{\dagger} \right) \exp(\kappa_{\mathrm{rd}}) \exp(-T') \\ &\quad \times [d_{\mathrm{s}}^{\kappa}, \ \exp(-\kappa_{\mathrm{rd}}) \tau_{\mu} \exp(\kappa_{\mathrm{rd}})] \exp(T') |\mathrm{HF}\rangle, \end{aligned} \tag{74}$$

$$\begin{aligned} A_{\mu\nu} &= \langle \mathrm{HF}| \tau_{\mu}^{\dagger} \exp(-T_{\mathrm{g}}) [H_{\mathrm{g}}^{\kappa}, \tau_{\nu}] \exp(T_{\mathrm{g}}) |\mathrm{HF}\rangle \\ &= \langle \mathrm{HF}| \tau_{\mu}^{\dagger} \exp(\kappa_{\mathrm{rd}}) \exp(-T') \\ &\quad \times [H_{\mathrm{s}}^{\kappa}, \ \exp(-\kappa_{\mathrm{rd}}) \tau_{\nu} \exp(\kappa_{\mathrm{rd}})] \exp(T') |\mathrm{HF}\rangle, \end{aligned} \tag{75}$$

$$\begin{aligned} F_{\mu\nu} &= \langle \mathrm{HF}| \left(1 + \sum_{\lambda} \overline{t}_{\lambda}^{\mathrm{g}} \tau_{\lambda}^{\dagger} \right) \exp(-T_{\mathrm{g}}) [[H_{\mathrm{g}}^{\kappa}, \tau_{\mu}], \tau_{\nu}] \\ &\quad \times \exp(T_{\mathrm{g}}) |\mathrm{HF}\rangle \\ &= \langle \mathrm{HF}| \left(1 + \sum_{\lambda} \overline{t}_{\lambda}^{\mathrm{g}} \tau_{\lambda}^{\dagger} \right) \exp(\kappa_{\mathrm{rd}}) \exp(-T') \\ &\quad \times [[H_{\mathrm{s}}^{\kappa}, e^{-\kappa_{\mathrm{rd}}} \tau_{\mu} e^{\kappa_{\mathrm{rd}}}], e^{-\kappa_{\mathrm{rd}}} \tau_{\nu} e^{\kappa_{\mathrm{rd}}}] \exp(T') |\mathrm{HF}\rangle. \end{aligned} \tag{76}$$

Since we here consider states that are invariant with respect to rotations among the occupied orbitals and among the virtual orbitals, we may instead of the projection manifold $\{\langle \mathrm{HF}| \tau_{\mu}^{\dagger} \exp(\kappa_{\mathrm{rd}})\}$ use the manifold $\{\langle \mathrm{HF}| \tau_{\mu}^{\dagger}\}$. Equation (72) and the matrix elements above then reduce to those of the symmetric connection so that the same result is obtained with the general and symmetric connections.

As shown in Ref. 30, the effective Hamiltonian in the symmetric connection H_{s} is gauge-origin independent. Gauge independence was the result of the gauge-origin independence of both the integrals over London orbitals and the connection matrix. It is straightforward to show that, in the symmetric connection, the effective dipole-moment operator is gauge-origin independent as well. As a consequence of the gauge independence of the effective Hamiltonian in the symmetric connection, the effective κ_{s} operator is gauge independent. Hence, H_{s}^{κ} and d_{s}^{κ} are gauge-origin independent, ensuring that the final result is gauge-origin independent.

F. The canonical formulation

We here consider the case where the Hartree–Fock orbitals are required to be canonical. The κ_{pq}^{g} matrix now contains both redundant and nonredundant orbital rotation parameters, which can be determined by solving the effective *canonical* equations,

$$\sum_{\sigma=\alpha,\beta}\langle \mathrm{HF}|[a_{q\sigma}^{\dagger},[a_{p\sigma},\ \exp(\kappa_{\mathrm{g}})H_{\mathrm{g}}\exp(-\kappa_{\mathrm{g}})]]_{+}|\mathrm{HF}\rangle = 2\,\delta_{pq}\epsilon_{p}, \tag{77}$$

where ϵ_p are the orbital energies. Note that, for the nonredundant parameters, the canonical condition is equivalent to the Hartree–Fock optimization condition in Eq. (52).[40]

Introducing Eq. (55), we find that the relaxed Hamiltonian $\exp(\kappa_{\mathrm{g}})H_{\mathrm{g}}\exp(-\kappa_{\mathrm{g}})$ in Eq. (77) can be rewritten in terms of the effective Hamiltonian in the symmetric connection as

$$\begin{aligned}\exp(\kappa_{\mathrm{g}})H_{\mathrm{g}}\exp(-\kappa_{\mathrm{g}}) &= \exp(\kappa_{\mathrm{g}})\exp(x_{\mathrm{g}})H_{\mathrm{s}} \\ &\quad\times\exp(-x_{\mathrm{g}})\exp(-\kappa_{\mathrm{g}}) \\ &= \exp(\kappa_{\mathrm{s}})H_{\mathrm{s}}\exp(-\kappa_{\mathrm{s}}).\end{aligned} \tag{78}$$

Inserting this expression in Eq. (77), we obtain the equations

$$\sum_{\sigma=\alpha,\beta}\langle \mathrm{HF}|[a_{q\sigma}^{\dagger},[a_{p\sigma},\ \exp(\kappa_{\mathrm{s}})H_{\mathrm{s}}\exp(-\kappa_{\mathrm{s}})]]_{+}|\mathrm{HF}\rangle = 2\,\delta_{pq}\epsilon_{p}, \tag{79}$$

which determine the κ_{pq}^{g} matrix in the symmetric connection. Comparing Eqs. (77) and (79), we find that the effective relaxed Hamiltonians in the general and symmetric connections are identical (even though the individual orbital parameters are not). The same necessarily applies for the relaxed dipole moment, as

$$\begin{aligned}d_{\mathrm{g}}^{\kappa} &= \exp(\kappa_{\mathrm{g}})d_{\mathrm{g}}\exp(-\kappa_{\mathrm{g}}) \\ &= \exp(\kappa_{\mathrm{g}})\exp(x_{\mathrm{g}})d_{\mathrm{s}}\exp(-x_{\mathrm{g}})\exp(-\kappa_{\mathrm{g}}) \\ &= \exp(\kappa_{\mathrm{s}})d_{\mathrm{s}}\exp(-\kappa_{\mathrm{s}}).\end{aligned} \tag{80}$$

Since the relaxed Hamiltonians determine the amplitudes according to

$$\begin{aligned}&\langle\mu|\exp(-T_{\mathrm{g}})H_{\mathrm{g}}^{\kappa}\exp(T_{\mathrm{g}})|\mathrm{HF}\rangle \\ &\quad\equiv\langle\mu|\exp(-T_{\mathrm{s}})H_{\mathrm{s}}^{\kappa}\exp(T_{\mathrm{s}})|\mathrm{HF}\rangle = 0,\end{aligned} \tag{81}$$

we conclude that the amplitudes obtained in the general and symmetric connections are identical. Therefore, all matrix elements to be differentiated (which always contain the relaxed operators) are the same in the general and symmetric connections.

The dependence of the final vector and matrix elements on only the symmetric connection integrals and rotation parameters indicates that, if a connection is chosen where the connection matrix is not gauge independent, for example, the *natural connection*,[37] then the gauge dependence introduced in the effective Hamiltonian through the connection matrix is cancelled in the effective *relaxed* Hamiltonian by the gauge-origin dependence of the effective orbital-rotation operator. This happens since the gauge dependence in the connection matrix may arise only from the $\boldsymbol{x}^{\mathrm{g}}$ matrix, which, together with the gauge dependent $\boldsymbol{\kappa}^{\mathrm{g}}$ matrix, defines the gauge independent $\boldsymbol{\kappa}^{\mathrm{s}}$ matrix.

IV. THE $\mathcal{B}$ TERM

The differentiation of the left transition moment with respect to the magnetic field leads to

$$\begin{aligned}\left.\frac{dM_{n\leftarrow j}^{d}}{dB}\right|_{0} &= [\boldsymbol{G}t^{m}(0)t^{d}(-\omega_{j})+\boldsymbol{F}^{m}t^{d}(-\omega_{j})+\boldsymbol{F}^{d}t^{m}(0) \\ &\quad+\eta^{d^{(B)}}]E^{j}(\omega_{j})+\overline{M}^{j}(\omega_{j})[\boldsymbol{A}^{d}t^{m}(0) \\ &\quad+\boldsymbol{A}^{m}t^{d}(-\omega_{j})+\boldsymbol{B}t^{m}(0)t^{d}(-\omega_{j})+\xi^{d^{(B)}}] \\ &\quad+\Delta\mathcal{W}_{nj}^{B}(0)\overline{M}^{j}(\omega_{j})t^{d}(-\omega_{j}) \\ &\quad+\overline{\xi}^{d}(-\omega_{j})\tilde{E}^{jm}(\omega_{j},0)+\overline{\xi}^{m}(0)E^{jd}(\omega_{j},-\omega_{j})\end{aligned} \tag{82}$$

and for the right transition moment we obtain

$$\left.\frac{dM_{j\leftarrow n}^{d}}{dB}\right|_{0} = \tilde{\bar{E}}^{jm}(-\omega_{j},0)\xi^{d}+\overline{E}^{j}(-\omega_{j})[\xi^{d^{(B)}}+\boldsymbol{A}^{d}t^{m}(0)]. \tag{83}$$

All vectors and matrices are now defined in the zero-field limit. The matrices $\boldsymbol{B}$, $\boldsymbol{G}$, $\boldsymbol{A}^{X}$, and $\boldsymbol{F}^{X}$, where X indicates the appropriate operator (component), are[26]

$$B_{\mu\nu\sigma} = \langle\overline{\mu}|[[H,\tau_{\nu}],\tau_{\sigma}]|\mathrm{CC}\rangle, \tag{84}$$

$$G_{\mu\nu\sigma} = \langle\Lambda|[[[H,\tau_{\mu}],\tau_{\nu}],\tau_{\sigma}]|\mathrm{CC}\rangle, \tag{85}$$

$$A_{\mu\nu}^{X} = \langle\overline{\mu}|[X,\tau_{\nu}]|\mathrm{CC}\rangle, \tag{86}$$

$$F_{\mu\nu}^{X} = \langle\Lambda|[[X,\tau_{\mu}],\tau_{\nu}]|\mathrm{CC}\rangle. \tag{87}$$

The superscript m in Eqs. (82) and (83) refers to the first-order two-electron magnetic perturbation operator

$$J^{(B)} = H^{(B)}+[\kappa^{(B)},H^{[0]}] = H^{[B]}+\{R^{(B)},H^{[0]}\}+[\kappa^{(B)},H^{[0]}], \tag{88}$$

that is, to the zero-field limit of the first derivative of the effective relaxed Hamiltonian H^{κ} with respect to the magnetic field strength; $d^{(B)}$ is the zero-field limit of the first derivative of the effective relaxed dipole operator d^{κ},

$$d^{(B)} = d^{[B]}+\{R^{(B)},d^{[0]}\}+[\kappa^{(B)},d^{[0]}]. \tag{89}$$

$H^{[B]}$ is analogous to the zero-order Hamiltonian ($H^{[0]}\equiv H$) where the undifferentiated integrals are replaced by the derivatives of the UMO integrals.[41] $\{R^{(B)},H^{[0]}\}$ is the effective operator defined on the one-index transformed integrals[41] $\{R^{(B)},h^{[0]}\}_{pq}$ and $\{R^{(B)},g^{[0]}\}_{pqrs}$. Similar definitions hold for $d^{(B)}$. If $\boldsymbol{R}$ is anti-Hermitian, $\{R,O\}\equiv[R,O]$. A detailed discussion of the relationship between the general and symmetric connection representations of the $J^{(B)}$ operator, which illustrates the discussion of Secs. III D–III F, is presented in the Appendix. A similar relationship is easily derived for

TABLE I. HF. CCSD results for the symmetry unique response contributions and the total Verdet constant at $\omega=0.113\,91$ a.u. Results labeled ''Unrelaxed'' refer to the use of the unrelaxed (one-electron) magnetic dipole moment operator on non-LAO basis sets. Results labeled ''Relaxed'' include the additional contributions due to the relaxation of the orbitals to the magnetic field. Results labeled ''London'' are those for the present reformulation of the Verdet constant according to Eq. (91). CM indicates the center of mass.

Basis	Gauge origin	$2V'_{xyz}$	$2V'_{yzx}$			$V(\omega)\times10^7$ a.u.[a]		
			Unrelaxed	Relaxed	London	Unrelaxed	Relaxed	London
cc-pVDZ	CM	0.797 74	1.5293	1.5218	1.3699	0.133 65	0.133 13	0.122 59
	H	0.797 74	0.858 29	0.874 07	1.3699	0.087 13	0.088 22	0.122 59
aug-cc-pVDZ	CM	2.5483	2.4940	2.4873	3.1094	0.261 16	0.260 70	0.303 81
	H	2.5483	2.2413	2.2696	3.1094	0.243 65	0.245 61	0.303 81
aug-cc-pVTZ	CM	2.6744	2.6801	2.6746	3.1188	0.278 43	0.278 05	0.308 83
	H	2.6744	2.4825	2.5150	3.1188	0.264 73	0.266 99	0.308 83
d-aug-cc-pVDZ	CM	3.2625	3.0922	3.0865	3.1984	0.327 37	0.326 97	0.334 73
	H	3.2625	3.1638	3.1970	3.1984	0.332 33	0.325 04	0.334 73
d-aug-cc-pVTZ	CM	3.1708	3.0591	3.0538	3.0499	0.321 90	0.321 53	0.321 26
	H	3.1708	3.0225	3.0586	3.0499	0.319 36	0.321 86	0.321 26

[a]Others: $0.219\,43\times10^{-7}$ a.u. (RPA); $0.220\,93\times10^{-7}$ a.u. (RPA/Becquerel). Origin at CM (Ref. 9).

$d^{(B)}$. The vector $E^{jd}(\omega_j,-\omega_j)$ is the first-order right excited state response to the electric-field perturbation, as defined in Ref. 32. The left and right vectors $\tilde{\bar{E}}^{jm}(\omega_j,0)$ and $\tilde{E}^{jm}(\omega_j,0)$ are the first-order responses to the magnetic field of the phase-isolated excitation vectors,[34] obtained from the derivative of the left and right eigenvectors with respect to the magnetic field strength. Thus, unlike the identification of the $\mathcal{B}$ term from the first residue of the dipole–dipole–magnetic dipole quadratic response function,[17] the present derivative formulation does not contain, *a priori*, unphysical singularities. $\Delta\mathcal{W}^{\mathcal{B}}_{nj}(0)$ is the first order response of the quasienergy difference between the state j and the ground state n with respect to the magnetic field strength.[34] The contribution with $\Delta\mathcal{W}^{\mathcal{B}}_{nj}(0)$ arises from the derivative of the intermediate vector. The complete expression for $\mathcal{B}$ can then readily be obtained by reintroducing the above derivatives in Eq. (14). If $\xi^{d^{(B)}}=\eta^{d^{(B)}}=0$ in Eqs. (82)–(83) and $J^{(B)}$ is substituted by the conventional one-electron magnetic dipole operator, the expression for the unrelaxed $\mathcal{B}$ term in a conventional (non-LAO) basis is obtained. The corresponding magnetic-field-relaxed expression is recovered removing all contributions from the $d^{[B]}$ operator, the connection matrix and the two-electron part of $H^{[B]}$.

V. THE VERDET CONSTANT

The resulting derivative of the polarizability is

$$\begin{aligned}\left.\frac{d\tilde{\alpha}_{\alpha\beta}(\omega_\alpha,\omega_\beta)}{dB}\right|_0 &= -\tfrac{1}{2}C^{\pm\omega}\{\boldsymbol{G}t^{d_\alpha}(\omega_\alpha)t^{d_\beta}(\omega_\beta)t^{m}(0)\\ &+\hat{P}^{d_\alpha d_\beta m}[\boldsymbol{F}^{d_\alpha}t^{d_\beta}(\omega_\beta)t^{m}(0)+\overline{t^{d}}^{\alpha}(\omega_\alpha)\boldsymbol{A}^{d_\beta}t^{m}(0)\\ &+\overline{t^{d}}^{\alpha}(\omega_\alpha)\boldsymbol{B}t^{d_\beta}(\omega_\beta)t^{m}(0)]+\hat{P}^{\alpha\beta}[\eta^{d^{(B)}_\alpha}t^{d_\beta}(\omega_\alpha)\\ &+\overline{t^{d}}^{\alpha}(\omega_\alpha)\xi^{d^{(B)}_\beta}]\},\end{aligned} \tag{90}$$

where $\hat{P}^{AB\cdots}[\cdots]$ indicates the sum over all permutations of the operators and relative frequencies in the expression inside the brackets, and $\omega_\alpha=-\omega_\beta=\omega$. The Verdet constant becomes

$$\begin{aligned}V(\omega)&=C\omega\epsilon_{\alpha\beta\gamma}\Im\left.\frac{d\tilde{\alpha}_{\alpha\beta}(\omega_\alpha,\omega_\beta)}{dB_\gamma}\right|_0\\ &=C\omega\epsilon_{\alpha\beta\gamma}\{\langle\langle d_\alpha;d_\beta,J^{(B_\gamma)}\rangle\rangle^{\mathrm{CC}}_{\omega_\beta,0}+\langle\langle d^{(B_\gamma)}_\alpha;d_\beta\rangle\rangle^{\mathrm{CC}}_{\omega_\beta}\\ &+\langle\langle d^{(B_\gamma)}_\beta;d_\alpha\rangle\rangle^{\mathrm{CC}}_{\omega_\alpha}\}=C\omega\epsilon_{\alpha\beta\gamma}V'_{\alpha\beta\gamma},\end{aligned} \tag{91}$$

where C collects the fundamental constants. In Eq. (91) the superscript CC is used to indicate that the three terms between curly brackets have the form of coupled cluster linear and quadratic response functions. Once again, if no magnetic field-dependent orbitals are used and no relaxation to the magnetic field is considered, all contributions from $d^{(B)}$ disappear, the operator $J^{(B)}$ reduces to the conventional one-electron magnetic dipole operator, and the usual unrelaxed quadratic response function expression for the Verdet constant is recovered.[9,11,12] The relaxed expression for non-LAO basis sets is obtained eliminating all contributions from $d^{[B]}$, from the connection matrix and from the two-electron part of the $H^{[B]}$ operator.

VI. PILOT RESULTS: THE VERDET CONSTANT OF HF AND H_2

Some pilot results for the Verdet constant of HF and H_2 at frequency $\omega=0.113\,91$ a.u. are collected in Tables I and II, respectively. They were obtained at the CCSD level, employing an integral direct implementation of the proposed approach within the coupled cluster (response) code of Refs. 31 and 42–45, which is interfaced to the DALTON package.[46] For a discussion of technical aspects of the implemention, we refer to later communications. Note that $V(\omega)$ of H_2 is gauge-origin independent by symmetry. As H_2 is a two-electron system, CCSD corresponds to full configuration interaction (FCI).

TABLE II. H_2. FCI results for the symmetry unique response contributions and the total Verdet constant at $\omega=0.113\,91$ a.u. Results labeled ''Unrelaxed'' refer to the use of the unrelaxed (one-electron) magnetic dipole moment operator on non-LAO basis sets. Results labeled ''Relaxed'' include the additional contributions due to the relaxation of the orbitals to the magnetic field. Results labeled ''London'' are those for the present reformulation of the Verdet constant according to Eq. (91).

		$2V'_{yzx}$			$V(\omega)\times 10^7$ a.u.[a]		
Basis	$2V'_{xyz}$	Unrelaxed	Relaxed	London	Unrelaxed	Relaxed	London
cc-pVDZ	0.11846	0.53365	0.53365	4.4736	0.04109	0.04109	0.31419
cc-pVTZ	0.70593	1.6685	1.6685	5.2498	0.14011	0.14011	0.38835
aug-cc-pVDZ	3.0727	4.2898	4.2898	5.4149	0.40383	0.40383	0.48181
aug-cc-pVTZ	3.6664	4.7127	4.7127	4.8100	0.45372	0.45372	0.46046
aug-cc-pVQZ	3.7022	4.7340	4.7340	4.7478	0.45644	0.45644	0.45739
aug-cc-pV5Z	3.6982	4.7293	4.7293	4.7312	0.45597	0.45597	0.45610
aug-cc-pV6Z	3.6950	4.7263	4.7263	4.7281	0.45565	0.45565	0.45578

[a]Others: $0.461\,39\times10^{-7}$ a.u. (RPA) (Ref. 9); $0.455\,56\times10^{-7}$ a.u. (James–Coolidge) (Ref. 13); $0.455\,62\times10^{-7}$ a.u. (FCI/d-aug-cc-pV5Z) (Ref. 12).

The value for the frequency was chosen among those employed in the experimental measurements by Ingersoll and Liebenberg,[47] as well as in other *ab initio* investigations.[9,12,13] Gauge-origin dependent results for $V(\omega)$ of HF at the center of mass obtained in the random-phase approximation (RPA) from the conventional quadratic response expression and from the approximate Becquerel/linear-response expression were presented in Ref. 9. Previous *ab initio* results for H_2 can be found in Refs. 9, 12, and 13. No experimental values for $V(\omega)$ of HF are available.

The tables include results for the two symmetry-unique response contributions V'_{xyz} and V'_{yzx}, as well as the final Verdet constant at the given frequency. The results labeled ''Unrelaxed'' are obtained from the conventional expression of the Verdet constant in terms of the unrelaxed one-electron magnetic dipole moment operator in perturbation independent basis sets.[9,11,12] The results labeled ''Relaxed'' are obtained by including also the contributions arising from the relaxation of the non-LAO orbitals to the magnetic field. Finally, results labeled ''London'' are those obtained according to Eq. (91) for a perturbation dependent basis of London orbitals and allowing for relaxation to the magnetic field.

Both molecules were placed with principal axis along the z axis. Because of the axial symmetry of the systems and this choice of geometrical setup, the orbitals are eigenfunctions of the angular momentum operator along the z axis, and the V'_{xyz} contribution is thus unaffected by the use of LAOs and/or the inclusion of orbital relaxation terms.

For HF, the V'_{yzx} component varies significantly when moving the gauge origin from the center of the nuclear masses (CM) to the H atom, both for the ''Unrelaxed'' and ''Relaxed'' cases. On the contrary gauge invariant results are obtained in the proposed derivative approach which employs London atomic orbitals (indicated by ''London''). The results for H_2 illustrate the effect of LAOs on the convergence of the V'_{yzx} component with the extension of the basis set. Note that within FCI the unrelaxed and relaxed results coincide.

VII. SUMMARY

We have presented a gauge-origin independent formulation of the Faraday $\mathcal{B}$ term of MCD and of the Verdet constant $V(\omega)$ of magneto-optical rotation, in terms of the first derivatives with respect to the magnetic field strength of gauge invariant CC response function expressions where the orbitals are allowed to relax in the magnetic field. Gauge invariance is ensured by this derivative reformulation and using the magnetic field-dependent basis of London orbitals. We have derived working expressions for CC wave functions in terms of the response of the cluster amplitudes and of the response vectors and matrices which are suitable for implementation in quantum chemical codes. This approach represents the first application of LAOs to the calculation of frequency-dependent quadratic response properties and can easily be extended to any frequency-dependent property that can be expressed as total derivative of a (frequency-dependent) functional with respect to the field strength of a *static* external magnetic perturbation—in other words, any property for which the frequency dependence is not associated with the magnetic field such as the hypermagnetizabilities in the Cotton–Mouton effect.[48,49] Pilot results for the Verdet constant of HF at the CCSD level were presented, clearly illustrating how the proposed approach guarantees the gauge-origin independence. Also, the effect of London orbitals on the convergence of the results with respect to the extension of the basis set was exemplified by results for the Verdet constant of H_2, which is gauge origin independent by symmetry. Details about the integral-direct implementation of the derived equations for the CCS, CC2, and CCSD models, and further numerical results will be presented in forthcoming communications.

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APPENDIX: THE FIRST-ORDER RELAXED HAMILTONIAN

The first-order relaxed Hamiltonian was defined in Eq. (88),

$$J^{(B)} = H^{(B)} + [\kappa^{(B)}, H^{[0]}] = H^{[B]} + \{R^{(B)}, H^{[0]}\} + [\kappa^{(B)}, H^{[0]}]. \quad \text{(A1)}$$

Partitioning the connection matrix $\boldsymbol{R}^{(B)}$ into a sum of Hermitian and anti-Hermitian components,

$$\boldsymbol{R}^{(B)} = \boldsymbol{R}_H^{(B)} + \boldsymbol{R}_A^{(B)} = \frac{\boldsymbol{R}^{(B)} + \boldsymbol{R}^{(B)\dagger}}{2} + \frac{\boldsymbol{R}^{(B)} - \boldsymbol{R}^{(B)\dagger}}{2}, \quad \text{(A2)}$$

$J^{(B)}$ may be rewritten as

$$J^{(B)} = H^{[B]} + \{R_H^{(B)}, H^{[0]}\} + [R_A^{(B)}, H^{[0]}] + [\kappa^{(B)}, H^{[0]}]. \quad \text{(A3)}$$

The Brillouin orbital optimization equation, Eq. (52), through first order may be expressed as

$$\begin{aligned}
&\langle \mathrm{HF}|[[\kappa^{(B)}, H^{[0]}], E_{ai}]|\mathrm{HF}\rangle \\
&\quad = -\langle \mathrm{HF}|[H^{(B)}, E_{ai}]|\mathrm{HF}\rangle \\
&\quad = -\langle \mathrm{HF}|[(H^{[B]} + \{R_H^{(B)}, H^{[0]}\}), E_{ai}]|\mathrm{HF}\rangle \\
&\qquad - \langle \mathrm{HF}|[[R_A^{(B)}, H^{[0]}], E_{ai}]|\mathrm{HF}\rangle. \quad \text{(A4)}
\end{aligned}$$

Dividing $R_A^{(B)}$ as

$$R_A^{(B)} = R_{A,\mathrm{rd}}^{(B)} + R_{A,\mathrm{nr}}^{(B)}, \quad \text{(A5)}$$

where $R_{A,\mathrm{rd}}^{(B)}(R_{A,\mathrm{nr}}^{(B)})$ has only nonvanishing parameters in the blocks that refer to the redundant (nonredundant) parameters of the orbital optimization we obtain

$$\begin{aligned}
&\langle \mathrm{HF}|[[\kappa_{HC}^{(B)}, H^{[0]}], E_{ai}]|\mathrm{HF}\rangle \\
&\quad = -\langle \mathrm{HF}|[(H^{[B]} + \{R_H^{(B)}, H^{[0]}\}), E_{ai}]|\mathrm{HF}\rangle, \quad \text{(A6)}
\end{aligned}$$

where

$$\boldsymbol{\kappa}_{HC}^{(B)} = \boldsymbol{\kappa}^{(B)} + \boldsymbol{R}_{A,\mathrm{nr}}^{(B)}. \quad \text{(A7)}$$

$\boldsymbol{\kappa}_{HC}^{(B)}$ is thus the solution for the ''Hermitian'' part of the orbital optimization condition, and we have used

$$\begin{aligned}
&\langle \mathrm{HF}|[[R_{A,\mathrm{rd}}^{(B)}, H^{[0]}], E_{ai}]|\mathrm{HF}\rangle \\
&\quad = \langle \mathrm{HF}|[[R_{A,\mathrm{rd}}^{(B)}, E_{ai}], H^{[0]}]|\mathrm{HF}\rangle \\
&\qquad + \langle \mathrm{HF}|[[E_{ai}, H^{[0]}], R_{A,\mathrm{rd}}^{(B)}]|\mathrm{HF}\rangle = 0, \quad \text{(A8)}
\end{aligned}$$

with $R_{A,\mathrm{rd}}^{(B)} = \Sigma_{st}^{\mathrm{red}} (R_{A,\mathrm{rd}}^{(B)})_{st} E_{st}$.

Inserting Eq. (A7) into Eq. (A3), we obtain

$$J^{(B)} = H^{[B]} + \{R_H^{(B)}, H^{[0]}\} + [\kappa_{HC}^{(B)}, H^{[0]}] + [R_{A,\mathrm{rd}}^{(B)}, H^{[0]}]. \quad \text{(A9)}$$

The first-order relaxed Hamiltonian thus depends only on the Hermitian part of the first-order connection matrix. In symmetric connection, $\boldsymbol{R}_H^{(B)} = -\frac{1}{2}\boldsymbol{S}^{(B)}$ and $\boldsymbol{R}_A^{(B)} = \boldsymbol{0}$. For any other connection—and in particular for the natural connection—we obtain

$$J^{(B)} = J_{\mathrm{s}}^{(B)} + [R_{A,\mathrm{rd}}^{(B)}, H^{[0]}], \quad \text{(A10)}$$

where $J_{\mathrm{s}}^{(B)}$ is the noncanonical first-order relaxed Hamiltonian for symmetric connection. The operators are thus identical except for a term involving rotations between the occupied and between the virtual orbitals.

In the canonical formulation, $\kappa^{(B)} = \sum_{pq}^{\mathrm{all}} \kappa_{pq}^{(B)} E_{pq}$ contains both redundant and nonredundant parameters, obtained solving the first order canonical condition,

$$\begin{aligned}
&\sum_{\sigma=\alpha,\beta} \langle \mathrm{HF}|[a_{q\sigma}^\dagger, [a_{p\sigma}, [\kappa^{(B)}, H^{[0]}]]]_+|\mathrm{HF}\rangle + 2\epsilon_p^{(B)}\delta_{pq} \\
&\quad = -\sum_{\sigma=\alpha,\beta} \langle \mathrm{HF}|[a_{q\sigma}^\dagger, [a_{p\sigma}, H^{(B)}]]_+|\mathrm{HF}\rangle. \quad \text{(A11)}
\end{aligned}$$

This can be rewritten as

$$\begin{aligned}
&\sum_{\sigma=\alpha,\beta} \langle \mathrm{HF}|[a_{q\sigma}^\dagger, [a_{p\sigma}, [\kappa_{HC}^{(B)}, H^{[0]}]]]_+|\mathrm{HF}\rangle + 2\epsilon_p^{(B)}\delta_{pq} \\
&\quad = -\sum_{\sigma=\alpha,\beta} \langle \mathrm{HF}|[a_{q\sigma}^\dagger, [a_{p\sigma}, (H^{[B]} \\
&\qquad + \{R_H^{(B)}, H^{[0]}\})]]_+|\mathrm{HF}\rangle, \quad \text{(A12)}
\end{aligned}$$

where, similar to previously,

$$R_A^{(B)} + \kappa^{(B)} = \kappa_{HC}^{(B)}. \quad \text{(A13)}$$

Inserting Eq. (A13) in Eq. (A3), we obtain

$$J^{(B)} = H^{[B]} + \{R_H^{(B)}, H^{[0]}\} + [\kappa_{HC}^{(B)}, H^{[0]}] \equiv J_{\mathrm{s}}^{(B)}, \quad \text{(A14)}$$

where $J_{\mathrm{s}}^{(B)}$ is the canonical first-order relaxed Hamiltonian for symmetric connection. Within the canonical formulation the first-order relaxed Hamiltonian in any general connection is completely identical to the first-order relaxed Hamiltonian in the symmetric connection.

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