Gauge-origin independent multiconfigurational self-consistent-field theory for vibrational circular dichroism

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Multiconfigurational self-consistent-field (MCSCF) theory is presented for the gauge-origin independent calculation of vibrational circular dichroism. Origin independence is attained by the use of London atomic orbitals (LAO). MCSCF calculations on ammonia and its isotopomer NHDT demonstrate that atomic axial tensors and vibrational rotational strengths converge fast with the size of the basis set when LAOs are used. The correlation effects are significant both for the atomic tensors and the vibrational rotational strengths even for the single configuration dominated NHDT molecule.

I. INTRODUCTION

The first vibrational circular dichroism (VCD) spectra were recorded in the early 1970s.[1] Since then VCD spectra have been reported for a large number of chiral systems. Parallel to and in interplay with the experimental developments the theoretical treatment of VCD has evolved. The experimental and theoretical developments before 1985 have been reviewed by Stephens and Lowe.[2]

The CD spectrum of a molecular transition is determined by its rotational strength, i.e., the imaginary part of the dot product of the electric and magnetic transition dipole moments. In the Born–Oppenheimer (BO) approximation the electronic contributions to the magnetic dipole moment vanish for a vibrational transition. By considering the first-order correction to the BO wave function, Stephens[3] determined in 1985 a nonvanishing contribution to the electronic magnetic moment and obtained in this way a rigorous description of VCD. Since 1985 the majority of theoretical papers on VCD has taken Stephens' equation as the starting point, and previous models have been analyzed in terms of this equation.[4–6]

The rotational strength is in Stephens' equation determined by atomic polar and axial tensors (APT and AAT), as well as the Cartesian to normal coordinate transformation matrix. The evaluation of atomic tensors requires differentiations with respect to the normal coordinates and the electromagnetic field. All but one of the *ab initio* implementations of Stephens' equation have been restricted to single-configurational wave functions. To obtain the differentiated quantities finite differences have been used[2,7] and more recently the coupled Hartree–Fock (CPHF) equations have been employed.[8] In an alternative approach, the atomic tensors have been written as sums over states and the random phase approximation (RPA) used for their evaluation.[6,9] Since the basis-set dependence on the molecular geometry has been neglected in these calculations, it has been necessary to use much larger basis sets than in

CPHF to achieve the same accuracy.[6] For a complete basis the two approaches give identical results.

The only *ab initio* calculation of VCD spectra that treats electron correlation is by Amos, Handy, and Palmieri on *R*-methylthiirane.[10] The normal modes and electric dipole derivatives were calculated at the second-order Møller–Plesset (MP2) level, but the derivatives with respect to the magnetic field were still obtained at the uncorrelated self-consistent-field (SCF) level. These authors conclude that correlation improves the theoretical description of VCD and the ability to carry out correlated VCD calculations is therefore important. We consider in this work the calculation of vibrational rotational strengths at the correlated multiconfigurational self-consistent-field (MCSCF) level using Stephens' equation.

Rotational strengths calculated from Stephens' equation are independent of the gauge origin for exact wave functions and for approximate wave functions expanded in a complete one-electron basis.[4] For finite basis sets, the calculations are not necessarily gauge independent. Much effort has been devoted to determine the optimum choice of gauge origin and basis sets.[11] In particular, the distributed origin (DO) gauge with origins distributed at the nuclei has proved to be favorable for calculations of AATs compared to calculations using a common origin (CO).[4,13,14] This scheme also has the advantage that vibrational rotational strengths are independent of the common gauge, although they depend on the choice of DOs. Recently the localized orbital/local origin (LORG) method, extensively used for nuclear shieldings, has been extended to VCD.[6]

The problem of gauge dependence is not restricted to VCD, but is common to all calculations involving an external magnetic field. To overcome this problem London[15] introduced field-dependent phase factors in the atomic orbitals for calculating magnetic susceptibilities. The current densities calculated using these so-called London atomic orbitals (LAO) [also termed the gauge-independent atomic orbitals (GIAO)] are gauge origin independent and

the calculated magnetic properties are therefore also independent of the origin.[16] The London phase factor is only but one of an infinite set of phase factors with this property. However, the London phase factor is optimal in the sense that for a one-center problem the LAO is correct through first order in the magnetic field, if the bare AO is an exact solution for the one-center problem without the magnetic field (see Appendix). It is therefore a natural choice for calculations using linear combinations of atomic orbitals.[16] LAOs have been used in SCF calculations of nuclear magnetic shieldings. The pioneering work was done by Ditchfield[17] and a modern SCF implementation was reported in 1990 by Wolinski et al.[18] Helgaker and Jørgensen have shown how the field dependence of the LAOs can be incorporated into the Hamiltonian, making the correlated calculation of gauge-independent properties straightforward.[19] In this work we demonstrate that the rotational strength and VCD spectra calculated from Stephens' equation are origin independent for MCSCF wave functions using LAOs. It is also shown that this is likewise true for other types of correlated wave functions.

Since atomic axial tensors depend on the origin even for exact wave functions, the origin independence of rotational strengths arises in a different way than it does for properties that may be identified with total derivatives of the electronic energy with respect to the magnetic field. Just as for exact wave functions, the origin independence of calculations using LAOs arises only when the dot product is taken between the electric and the magnetic transition moments.

We present SCF and MCSCF calculations of atomic tensors and vibrational rotational strengths for the ground state of the ammonia isotopomer NHDT. Basis set effects are investigated by applying a range of systematically increased basis sets, and the importance of using LAOs is illustrated by comparing the results to calculations using conventional AOs. Correlation effects are illuminated by comparing the uncorrelated SCF results to the correlated MCSCF results. Complete active space (CAS) wave functions are used in the MCSCF calculations and two levels of correlation are considered.

II. THEORY

The intensity of VCD assigned to the vibrational transition $g \rightarrow e$ is determined by the rotational strength

$$R(g \rightarrow e) = \text{Im}[\langle g | \mu_{\text{el}} | e \rangle \langle e | \mu_{\text{mag}} | g \rangle], \quad (1)$$

where μ_{el} and μ_{mag} are the electronic and magnetic dipole operators

$$\mu_{\text{el}} = -\sum_i \mathbf{r}_i + \sum_M Z_M \mathbf{R}_M, \quad (2)$$

$$\mu_{\text{mag}} = -\frac{1}{2} \sum_i \mathbf{r}_i \times \mathbf{p}_i + \sum_M \left(\frac{Z_M}{2M_M}\right) \mathbf{R}_M \times \mathbf{P}_M. \quad (3)$$

Here $\mathbf{r}_i$ and $\mathbf{p}_i$ are the position and momentum of the ith electron, and Z_M, M_M, $\mathbf{R}_M$, and $\mathbf{P}_M$ are the charge, mass, position, and momentum of the Mth nucleus in atomic units. The assumption of harmonicity and other approxi-

mations lead to Stephens' equation for the vibrational rotational strength of a fundamental transition in the nth normal mode[3]

$$R(0 \rightarrow 1)_n = \text{Im}[\widetilde{\mathbf{P}}_n \cdot \widetilde{\mathbf{M}}_n], \quad (4)$$

where

$$\widetilde{P}_{n,\beta} \equiv \sum_{M\alpha} P_{M\alpha,\beta} S_{M\alpha,n},$$

$$\widetilde{M}_{n,\beta} \equiv \sum_{M\alpha} M_{M\alpha,\beta} S_{M\alpha,n}, \quad (5)$$

with $S_{M\alpha,n}$ being the Cartesian to normal coordinate transformation matrix. The subscript M labels the nuclei and α their Cartesian coordinates. The index β of $\widetilde{P}_{n,\beta}$ and $\widetilde{M}_{n,\beta}$ refers to the Cartesian components of the magnetic and electric dipole operators. The atomic polar tensor is defined as

$$P_{M\alpha,\beta} \equiv E_{M\alpha,\beta} + N_{M\alpha,\beta}, \quad (6)$$

where

$$E_{M\alpha,\beta} \equiv \frac{\partial \langle \widetilde{0}(\mathbf{R}) | -\Sigma_i r_{i\beta} | \widetilde{0}(\mathbf{R}) \rangle}{\partial R_{M\alpha}} \bigg|_{\mathbf{R}=\mathbf{R}_0}, \quad (7)$$

$$N_{M\alpha,\beta} \equiv Z_M \delta_{\alpha\beta}. \quad (8)$$

The electronic ground state at the nuclear geometry $\mathbf{R}$ is denoted $|\widetilde{0}(\mathbf{R})\rangle$. $\mathbf{R}_0$ is the equilibrium geometry and $R_{M\alpha}$ and $r_{i\beta}$ are the nuclear and electronic Cartesian coordinates. The atomic axial tensor is given by

$$M_{M\alpha,\beta} \equiv I_{M\alpha,\beta} + J_{M\alpha,\beta}, \quad (9)$$

where

$$I_{M\alpha,\beta} \equiv \left\langle \frac{\partial \widetilde{0}(\mathbf{R})}{\partial R_{M\alpha}} \bigg| \frac{\partial \widetilde{0}(\mathbf{B})}{\partial B_\beta} \right\rangle \bigg|_{\substack{\mathbf{R}=\mathbf{R}_0 \\ \mathbf{B}=0}}, \quad (10)$$

$$J_{M\alpha,\beta} \equiv \frac{i}{4} \sum_\gamma \epsilon_{\alpha\beta\gamma} Z_M R_{0M\gamma}. \quad (11)$$

Here B_β is a component of the magnetic field $\mathbf{B}$ and $R_{0M\gamma}$ a Cartesian component of the equilibrium position of nucleus M. $\epsilon_{\alpha\beta\gamma}$ is the antisymmetric unit third-rank tensor.

When calculating vibrational rotational strengths from Stephens' equation, we must evaluate the expressions Eqs. (7) and (10). We here derive their explicit form for MCSCF wave functions. Since these equations involve the derivatives of the electronic ground state with respect to the nuclear coordinates and the magnetic field, we first consider the derivative of a MCSCF state with respect to a general perturbational parameter. The resulting expression is used to evaluate the expectation value of a differentiated one-electron operator and also the overlap between differentiated MCSCF states, and from these equations the atomic tensors are calculated. Provided London orbitals are used, we show that the calculated vibrational rotational strengths are gauge invariant and that this invariance also holds for other wave functions.

A. Differentiating the MCSCF wave function with respect to a parameter

The MCSCF wave function is constructed from a set of one-electron basis functions (BFs) $\omega_\mu(\mathbf{r};\mathbf{P})$ that are functions of the electronic coordinates $\mathbf{r}$ and depend parametrically on a set of parameters $\mathbf{P}$. For ease of notation we write $\omega_\mu(P)$, omitting the electronic coordinates. An orthonormal set of molecular orbitals (MOs) is expanded in the set of BFs,

$$\widetilde{\varphi}_i(P) = \sum_\mu K_{\mu i}(P)\omega_\mu(P). \tag{12}$$

The coefficients $K_{\mu i}(P)$ must depend on P since otherwise the MOs cannot be orthonormal at all P.

Assuming that the optimized MOs are known for a given reference value P_0 of the parameter P, a new set of unmodified molecular orbitals (UMOs) may be generated at P according to the expression

$$\psi_i(P) = \sum_\mu K_{\mu i}(P_0)\omega_\mu(P). \tag{13}$$

The UMO coefficients are equal to the MO coefficients at P_0 and therefore independent of P. Hence the UMOs are in general not orthonormal

$$S_{ij}(P) \equiv \langle \psi_i(P) | \psi_j(P) \rangle$$

$$= \sum_{\mu\nu} K_{\mu i}^*(P_0) K_{\nu j}(P_0)\langle \omega_\mu(P) | \omega_\nu(P) \rangle \neq \delta_{ij}. \tag{14}$$

However, from the UMOs a new set of orthonormalized molecular orbitals (OMOs) can be constructed as

$$\varphi_i(P) \equiv \sum_j T_{ji}(P)\psi_j(P), \tag{15}$$

where $\mathbf{T}(P)$ is the so-called connection matrix. Provided the UMO overlap matrix $\mathbf{S}(P)$ Eq. (14) is nonsingular, symmetric orthonormalization is defined by setting $\mathbf{T}(P)$ equal to $\mathbf{S}^{-1/2}(P)$. Note that although the OMOs are obtained from the MOs which have been optimized at P_0, the OMOs themselves have *not* been reoptimized at P.

We thus distinguish between the UMOs which are neither orthonormal nor optimized, the OMOs which are orthonormal but not optimized, and the MOs which are both orthonormal and optimized. The UMOs at P are obtained from the optimized MOs at P_0, the OMOs are then obtained by orthonormalizing the UMOs, and finally the MOs at P are obtained by optimizing the OMOs. At the reference value P_0 all three sets are identical.

In second quantization we assign to each OMO a creation operator $a_i^+(P)$ that creates an electron in the orbital $\varphi_i(P)$ when acting on the vacuum state $|\text{vac}\rangle$.[20] Ordered products of the creation operators generate Slater determinants at P

$$|\phi_g^S(P)\rangle = \prod_{i \in S_g} a_i^+(P)|\text{vac}\rangle. \tag{16}$$

Configuration state functions (CSFs) $|\phi_g(P)\rangle$ are simple linear combinations of the Slater determinants.

At P_0 an optimized reference state is generated as linear combinations of CSFs,

$$|0(P_0)\rangle = \sum_g C_{g0}(P_0)|\phi_g(P_0)\rangle. \tag{17}$$

The configuration interaction (CI) coefficients $C_{g0}(P_0)$ and MO coefficients $K_{i\mu}(P_0)$ define the reference state at P_0 and are optimized according to the generalized Brillouin theorem

$$\langle 0(P_0)|[E_{ij}(P_0),H_0(P_0)]|0(P_0)\rangle = 0,$$
$$\langle 0(P_0)|[R_r^+(P_0),H_0(P_0)]|0(P_0)\rangle = 0. \tag{18}$$

Here $H_0(P_0)$ is the electronic Hamiltonian and

$$E_{ij}(P) \equiv a_i^+(P)a_j(P), \tag{19}$$

$$R_r^+(P) \equiv |r(P)\rangle\langle 0(P)|, \quad |r(P)\rangle \neq |0(P)\rangle \tag{20}$$

are the excitation and state transfer operators. In Eq. (18) the subscripts $i > j$ label nonredundant rotations only. The annihilation operator $a_j(P)$ is the adjoint of $a_j^+(P)$ and $|r(P)\rangle$ belongs to the orthonormal manifold spanned by the CSFs used to generate the reference state. The states $|r(P)\rangle$ are orthogonal to the reference state and the indices r referring to these states are positive. In addition to $R_r^+(P)$ we define

$$R_{-r}^+(P) \equiv |0(P)\rangle\langle r(P)| \tag{21}$$

which will prove convenient later.

The CI coefficients optimized at P_0 define for all P a normalized but *not* optimized reference state

$$|0(P)\rangle = \sum_g C_{g0}(P_0)|\phi_g(P)\rangle. \tag{22}$$

The optimized state at P is obtained by applying a unitary transformation to $|0(P)\rangle$,

$$|\widetilde{0}(P)\rangle = \exp[i\kappa(P)]\exp[iS(P)]|0(P)\rangle. \tag{23}$$

The Hermitian operators $\kappa(P)$ and $S(P)$ are defined by

$$\kappa(P) \equiv \sum_{i \neq j} \kappa_{ij}(P)E_{ij}(P), \tag{24}$$

$$S(P) \equiv \sum_r S_r(P)R_r^+(P), \tag{25}$$

where the amplitudes of the orbital excitation and state transfer operators obey

$$\kappa_{ji}(P) = \kappa_{ij}^*(P)$$

and

$$S_{-r}(P) = S_r^*(P) \tag{26}$$

and the amplitudes $\kappa_{ij}(P)$ and $S_r(P)$ determine the optimized state at P. The summation in Eq. (24) is over nonredundant rotations and in Eq. (25) the summation is over

both positive and negative indices excluding the reference state 0. This convention for sums over r is used in the remainder of this paper.

The parametrization of the optimized reference state is now established and we can take the derivative of the state with respect to a general parameter P,

$$\frac{\partial}{\partial P}|\tilde{0}\rangle = \left\{ i \sum_{i \neq j} \kappa_{ij}^{(P)} E_{ij} + i \sum_r S_r^{(P)} R_r^+ + \sum_i \frac{\partial a_i^+}{\partial P} a_i \right\} |0\rangle. \tag{27}$$

Here the derivatives are evaluated at P_0 but to simplify notation we omit the argument P for all terms evaluated at P_0. The derivatives of the amplitudes with respect to P are

$$\kappa_{ij}^{(P)} \equiv \frac{\partial \kappa_{ij}}{\partial P}$$

and

$$S_r^{(P)} \equiv \frac{\partial S_r}{\partial P}. \tag{28}$$

The differentiated creation operator $\partial a_i^+(P)/\partial P$ in Eq. (27) creates an electron in $\partial \varphi_i(P)/\partial P$. This orbital can be separated into two parts, one spanned by the OMOs at P and one orthogonal to the OMOs. With the orthogonal part written as $\varphi_{\perp i}^{(P)}(P)$, the differentiated OMO reads

$$\frac{\partial \varphi_i(P)}{\partial P} = \sum_j D_{ji}^{(P)}(P) \varphi_j(P) + \varphi_{\perp i}^{(P)}(P). \tag{29}$$

Thus with $a_{\perp i}^{(P)+}(P)$ being the operator that creates an electron in $\varphi_{\perp i}^{(P)}(P)$, the differentiated creation operator is

$$\frac{\partial a_i^+(P)}{\partial P} = \sum_j D_{ji}^{(P)}(P) a_j^+(P) + a_{\perp i}^{(P)+}(P). \tag{30}$$

Multiplying Eq. (29) by an OMO and integrating over electronic coordinates, the expansion coefficients are seen to be

$$D_{ji}^{(P)}(P) = \left\langle \varphi_j(P) \left| \frac{\partial \varphi_i(P)}{\partial P} \right\rangle \right. \tag{31}$$

and for $P = P_0$,

$$D_{ji}^{(P)} = \left\langle \psi_j \left| \frac{\partial \psi_i}{\partial P} \right\rangle + \frac{\partial T_{ji}}{\partial P}. \right. \tag{32}$$

We now assume that symmetrical orthonormalization is used such $\mathbf{T}(P)$ is equal to $\mathbf{S}^{-1/2}(P)$. Since $\mathbf{S}(P_0)$ is the identity matrix and

$$\mathbf{S}^{-1/2}(P) = \exp\left[-\tfrac{1}{2} \ln \mathbf{S}(P) \right], \tag{33}$$

where

$$\ln \mathbf{S}(P) = [\mathbf{S}(P) - 1] - \frac{[\mathbf{S}(P) - 1]^2}{2}$$
$$+ \frac{[\mathbf{S}(P) - 1]^3}{3} - \cdots \tag{34}$$

we find that

$$\frac{\partial T_{ji}}{\partial P} = -\frac{1}{2} \frac{\partial}{\partial P} \langle \psi_j | \psi_i \rangle. \tag{35}$$

At $P = P_0$ we see that the expansion coefficients for the differentiated OMOs are

$$D_{ji}^{(P)} = \frac{1}{2} \left(\left\langle \psi_j \left| \frac{\partial \psi_i}{\partial P} \right\rangle - \left\langle \frac{\partial \psi_j}{\partial P} \right| \psi_i \right\rangle \right)$$
$$= \frac{1}{2} \sum_{\mu\nu} K_{\mu j}^* K_{\nu i} \left(\left\langle \omega_\mu \left| \frac{\partial \omega_\nu}{\partial P} \right\rangle - \left\langle \frac{\partial \omega_\mu}{\partial P} \right| \omega_\nu \right\rangle \right) \tag{36}$$

and thus define an anti-Hermitian matrix $D_{ij}^{(P)} = -D_{ji}^{(P)*}$.

We insert Eq. (30) into Eq. (27) and obtain

$$\frac{\partial}{\partial P}|\tilde{0}\rangle = \left\{ i \sum_{i,j} [\kappa_{ij}^{(P)} - iD_{ij}^{(P)}] E_{ij} + i \sum_r S_r^{(P)} R_r^+ \right.$$
$$\left. + \sum_i a_{\perp i}^{(P)+} a_i \right\} |0\rangle \tag{37}$$

which is the final expression valid for the derivative of an optimized reference state with respect to an arbitrary parameter P. The derivative has been rewritten in the form of the effective differentiation operator in the curly brackets on the right-hand side. Although the first sum is over all i and j, the amplitudes $\kappa_{ij}^{(P)}$ are defined only for nonredundant rotations and $\kappa_{ij}^{(P)}$ is therefore zero for all redundant rotations. Equation (37) is a generalization of Eq. (24) derived by Bak *et al.* for calculations of first-order nonadiabatic coupling matrix elements.[21]

B. Matrix elements involving differentiation with respect to a parameter

In second quantization the expectation value of an arbitrary one-electron operator is given as

$$\sum_{ij} \langle \varphi_i | f | \varphi_j \rangle \langle \tilde{0} | E_{ij} | \tilde{0} \rangle. \tag{38}$$

Using the result of the previous section, we now take the derivative of this expression. From Eqs. (15) and (35) it is found that the first factor in Eq. (38) gives

$$\frac{\partial}{\partial P} \langle \varphi_i | f | \varphi_j \rangle$$
$$= \left\langle \frac{\partial \psi_i}{\partial P} \left| f \right| \psi_j \right\rangle + \left\langle \psi_i \left| f \right| \frac{\partial \psi_j}{\partial P} \right\rangle + \langle \psi_i | f^{(P)} | \psi_j \rangle$$
$$- \frac{1}{2} \sum_k \left(\frac{\partial S_{kj}}{\partial P} \langle \psi_i | f | \psi_k \rangle + \frac{\partial S_{ik}}{\partial P} \langle \psi_k | f | \psi_j \rangle \right), \tag{39}$$

where we use the notation

$$f^{(P)} \equiv \frac{\partial f}{\partial P}. \tag{40}$$

Differentiating the second factor in Eq. (38) we obtain

$$\frac{\partial}{\partial P}\langle\tilde{0}|E_{ij}|\tilde{0}\rangle = \sum_{kl} i\kappa_{kl}^{(P)}\langle 0|[E_{ij},E_{kl}]|0\rangle$$

$$+ \sum_{r} iS_{r}^{(P)}\langle 0|[E_{ij},R_{r}^{+}]|0\rangle. \quad (41)$$

The identity

$$[E_{ij},E_{kl}] = \delta_{jk}E_{il} - \delta_{li}E_{kj} \quad (42)$$

as well as Eqs. (30), (36), and (37) have been used to arrive at Eq. (41). Combining Eqs. (39) and (41), the differentiated expectation value at P_0 is seen to be

$$\frac{\partial}{\partial P}\sum_{ij}\langle\varphi_i|f|\varphi_j\rangle\langle\tilde{0}|E_{ij}|\tilde{0}\rangle = \sum_{ij}\sum_{r} iS_{r}^{(P)}\langle\psi_i|f|\psi_j\rangle\langle 0|[E_{ij},R_{r}^{+}]|0\rangle + \sum_{ijkl} i\kappa_{kl}^{(P)}\langle\psi_i|f|\psi_j\rangle\langle 0|[E_{ij},E_{kl}]|0\rangle$$

$$+ \sum_{ij}\left\{\left[\left\langle\frac{\partial\psi_i}{\partial P}\Big|f\Big|\psi_j\right\rangle + \left\langle\psi_i\Big|f\Big|\frac{\partial\psi_j}{\partial P}\right\rangle + \langle\psi_i|f^{(P)}|\psi_j\rangle\right]\langle 0|E_{ij}|0\rangle\right\}$$

$$-\frac{1}{2}\sum_{ij}\left\{\sum_{k}\left[\frac{\partial S_{ik}}{\partial P}\langle\psi_k|f|\psi_j\rangle + \frac{\partial S_{kj}}{\partial P}\langle\psi_i|f|\psi_k\rangle\right]\langle 0|E_{ij}|0\rangle\right\}. \quad (43)$$

This equation will be used to derive an explicit expression for the electric dipole moment differentiated with respect to a nuclear coordinate, but first we derive an expression for the overlap between differentiated wave functions.

The matrix element between the reference state differentiated with respect to P at P_0 and with respect to Q at Q_0 is found from Eq. (37),

$$\left\langle\frac{\partial\tilde{0}}{\partial Q}\Big|\frac{\partial\tilde{0}}{\partial P}\right\rangle$$

$$= \sum_{i,j,k,l}\langle 0|E_{ij}E_{kl}|0\rangle[\kappa_{ij}^{(Q)}-iD_{ij}^{(Q)}][\kappa_{kl}^{(P)}-iD_{kl}^{(P)}]$$

$$+ \sum_{i,j}\sum_{r}\langle 0|E_{ij}R_{r}^{+}|0\rangle[\kappa_{ij}^{(Q)}-iD_{ij}^{(Q)}]S_{r}^{(P)}$$

$$+ \sum_{i,j}\sum_{r}\langle 0|R_{r}^{+}E_{ij}|0\rangle S_{r}^{(Q)}[\kappa_{ij}^{(P)}-iD_{ij}^{(P)}]$$

$$+ \sum_{r>0}S_{r}^{(Q)*}S_{r}^{(P)} + \sum_{i,j}\langle 0|E_{ij}|0\rangle\langle\varphi_{\perp i}^{(Q)}|\varphi_{\perp j}^{(P)}\rangle. \quad (44)$$

We have used the fact that

$$[a_i(P),a_{\perp j}^{(P)+}(P)]_{+} = \langle\varphi_i(P)|\varphi_{\perp j}^{(P)}(P)\rangle = 0 \quad (45)$$

and also

$$\langle 0|a_i^{+}a_{\perp i}^{(Q)}a_{\perp j}^{(P)+}a_j|0\rangle = \langle 0|a_i^{+}a_j|0\rangle[a_{\perp i}^{(Q)},a_{\perp j}^{(P)+}]_{+}$$

$$= \langle 0|E_{ij}|0\rangle\langle\varphi_{\perp i}^{(Q)}|\varphi_{\perp j}^{(P)}\rangle. \quad (46)$$

From Eqs. (29) and (36) we evaluate the last integral in Eq. (44) as

$$\langle\varphi_{\perp i}^{(Q)}|\varphi_{\perp j}^{(P)}\rangle = \left\langle\frac{\partial\varphi_i}{\partial Q}\Big|\frac{\partial\varphi_j}{\partial P}\right\rangle - \sum_{k}D_{ki}^{(Q)*}D_{kj}^{(P)}$$

$$= \left\langle\frac{\partial\psi_i}{\partial Q}\Big|\frac{\partial\psi_j}{\partial P}\right\rangle - \sum_{k}\left\langle\frac{\partial\psi_i}{\partial Q}\Big|\psi_k\right\rangle\left\langle\psi_k\Big|\frac{\partial\psi_j}{\partial P}\right\rangle$$

$$= \sum_{\mu\nu}K_{\mu i}^{*}K_{\nu j}\left[\left\langle\frac{\partial\omega_\mu}{\partial Q}\Big|\frac{\partial\omega_\nu}{\partial P}\right\rangle\right.$$

$$\left. - \sum_{\rho\delta}\sum_{k}K_{\rho k}K_{\delta k}^{*}\left\langle\frac{\partial\omega_\mu}{\partial Q}\Big|\omega_\rho\right\rangle\left\langle\omega_\delta\Big|\frac{\partial\omega_\nu}{\partial P}\right\rangle\right] \quad (47)$$

which is our final expression of the overlap between two differential wave functions.

C. The vibrational rotational strength for a MCSCF wave function

The formulas derived in Sec. II B will now be used to calculate the atomic tensors Eqs. (6) and (9), which define the vibrational rotational strength for a MCSCF wave function. The amplitudes in Eqs. (24) and (25) define the unitary transformation operator in Eq. (23) and may be split into real and imaginary parts

$$\kappa_{ij} = \kappa_{ij}^{R} + i\kappa_{ij}^{I}$$

and

$$S_r = S_r^{R} + iS_r^{I} \quad (48)$$

which according to Eq. (26) obey

$$\kappa_{ji}^{R} = \kappa_{ij}^{R}, \quad \kappa_{ji}^{I} = -\kappa_{ij}^{I}, \quad S_{-r}^{R} = S_r^{R}, \quad \text{and} \quad S_{-r}^{I} = -S_r^{I}. \quad (49)$$

For real transformations the amplitudes become

$$\kappa_{ij} = i\kappa_{ij}^{I}$$

and

$$S_r = iS_r^{I} \quad (50)$$

and for imaginary transformations

$$\kappa_{ij} = \kappa_{ij}^{R}$$

and

$$S_r = S_r^{R}. \quad (51)$$

We take the reference wave function to be real. A nuclear displacement results in a real perturbation and the associated unitary transformation must be real. In contrast, the first-order perturbation induced by a magnetic field is imaginary and the associated first-order transformation is imaginary.[19] Therefore the first term in the APT is found from Eqs. (43), (49), and (50) to be

$$E_{M\alpha,\beta} = -\frac{\partial}{\partial R_{M\alpha}} \sum_{ij} \langle \varphi_i | r_\beta | \varphi_j \rangle \langle \tilde{0} | E_{ij} | \tilde{0} \rangle$$

$$= \sum_{ij} \sum_r S_r^{I(R_{M\alpha})} \langle \psi_i | r_\beta | \psi_j \rangle \langle 0 | [E_{ij}, R_r^+] | 0 \rangle$$

$$+ \sum_{ijkl} \kappa_{kl}^{I(R_{M\alpha})} \langle \psi_i | r_\beta | \psi_j \rangle \langle 0 | [E_{ij}, E_{kl}] | 0 \rangle$$

$$- \sum_{ij} \left\{ \left[2 \left\langle \frac{\partial \psi_i}{\partial R_{M\alpha}} \middle| r_\beta \middle| \psi_j \right\rangle \right. \right.$$

$$\left. \left. - \sum_k \frac{\partial S_{ik}}{\partial R_{M\alpha}} \langle \psi_k | r_\beta | \psi_j \rangle \right] \langle 0 | E_{ij} | 0 \rangle \right\}. \quad (52)$$

An expression equivalent to Eq. (52) has been derived in a different way by Helgaker and Jørgensen.[22] The electronic contribution to the AAT is found from Eqs. (44) and (49)–(51),

$$I_{M\alpha,\beta} = \left\langle \frac{\partial \tilde{0}}{\partial R_{M\alpha}} \middle| \frac{\partial \tilde{0}}{\partial B_\beta} \right\rangle = \sum_{i,j,k,l} \langle 0 | E_{ij} E_{kl} | 0 \rangle [\kappa_{ij}^{I(R_{M\alpha})} - D_{ij}^{(R_{M\alpha})}][i\kappa_{kl}^{R(B_\beta)} + D_{kl}^{(B_\beta)}] + \sum_{i,j} \sum_r \langle 0 | R_r^+ E_{ij} | 0 \rangle S_r^{I(R_{M\alpha})}$$

$$\times [i\kappa_{ij}^{R(B_\beta)} + D_{ij}^{(B_\beta)}] + i \sum_{i,j} \sum_r \langle 0 | E_{ij} R_r^+ | 0 \rangle [\kappa_{ij}^{I(R_{M\alpha})} - D_{ij}^{(R_{M\alpha})}] S_r^{R(B_\beta)}$$

$$- i \sum_{r>0} S_r^{I(R_{M\alpha})} S_r^{R(B_\beta)} + \sum_{i,j} \langle 0 | E_{ij} | 0 \rangle \langle \varphi_{\perp i}^{(R_{M\alpha})} | \varphi_{\perp j}^{(B_\beta)} \rangle. \quad (53)$$

Equations (52) and (53) are the formulas to be used when the vibrational rotational strengths of fundamental transitions are calculated from MCSCF wave functions. Together with Eqs. (13), (36), and (47) these equations expresses $E_{M\alpha,\beta}$ and $I_{M\alpha,\beta}$ as sums of density matrices multiplied with BFs integrals and derivative orbital and CSF amplitudes. The derivative amplitudes are found from response equations as described by Helgaker and Jørgensen.[19,22]

D. London atomic orbitals

The one-electron BFs are chosen as LAO (see Appendix)[15]

$$\omega_\mu = \exp(-iA_M^e \cdot r) \chi_\mu. \quad (54)$$

Here $\chi_\mu = \chi_\mu(r_M)$ is an atomic orbital centered on nucleus M with position R_M. The vector potential A_M^e represents the external magnetic field B at R_M,

$$A_M^e = \tfrac{1}{2} B \times R_{MO}, \quad R_{MO} = R_M - O, \quad (55)$$

where O is the gauge origin. Differentiating the LAOs with respect to B we obtain

$$\frac{\partial \omega_\mu}{\partial B} = -\frac{i}{2}(R_{MO} \times r) \omega_\mu. \quad (56)$$

Introducing the antisymmetric matrix

$$Q^{MO} \equiv \begin{pmatrix} 0 & -Z_{MO} & Y_{MO} \\ Z_{MO} & 0 & -X_{MO} \\ -Y_{MO} & X_{MO} & 0 \end{pmatrix} \quad (57)$$

we may write the cross product in Eq. (56) as a matrix multiplication

$$R_{MO} \times r = Q^{MO} r. \quad (58)$$

Inserting Eqs. (54) and (56) in Eqs. (36) and (47), we obtain at zero field

$$D_{ji}^{(B_\beta)} = -\frac{i}{4} \sum_{\mu\nu} K_{\mu j} K_{\nu i} (Q_\beta^{MO} + Q_\beta^{NO}) \langle \chi_\mu | r | \chi_\nu \rangle \quad (59)$$

and

$$\langle \varphi_{\perp i}^{(R_{M\alpha})} | \varphi_{\perp j}^{(B_\beta)} \rangle$$

$$= -\frac{i}{2} \sum_{\mu\nu} Q_\beta^{NO} \cdot K_{\mu i} K_{\nu j} \left\{ \left\langle \frac{\partial \chi_\mu}{\partial R_{M\alpha}} \middle| r \middle| \chi_\nu \right\rangle \right.$$

$$\left. - \sum_{\rho\delta} \sum_k K_{\rho k} K_{\delta k} \left\langle \frac{\partial \chi_\mu}{\partial R_{M\alpha}} \middle| \chi_\rho \right\rangle \langle \chi_\delta | r | \chi_\nu \rangle \right\}, \quad (60)$$

where Q_β^{MO} is the βth row of Q^{MO} and where R_{NO} in Q_β^{NO} is defined for χ_ν in the same way as R_{MO} is defined for χ_μ. Since $D_{kl}^{(B_\beta)}$ is imaginary and $D_{ij}^{(R_{M\alpha})}$ is real, the electronic part of AAT can be rewritten as

$$I_{M\alpha,\beta} = \left\langle \frac{\partial \tilde{0}}{\partial R_{M\alpha}} \middle| \frac{\partial \tilde{0}}{\partial B_\beta} \right\rangle = \frac{1}{2} \sum_{i,j,k,l} \langle 0 | [E_{ij}, E_{kl}] | 0 \rangle [\kappa_{ij}^{I(R_{M\alpha})} - D_{ij}^{(R_{M\alpha})}] [i\kappa_{kl}^{R(B_\beta)} + D_{kl}^{(B_\beta)}] + \frac{1}{2} \sum_{ij} \sum_r (\langle 0 | [R_r^+, E_{ij}] | 0 \rangle$$

$$\times \{ S_r^{I(R_{M\alpha})} [i\kappa_{ij}^{R(B_\beta)} + D_{ij}^{(B_\beta)}] - i[\kappa_{ij}^{I(R_{M\alpha})} - D_{ij}^{(R_{M\alpha})}] S_r^{R(B_\beta)} \})$$

$$- i \sum_{r>0} S_r^{I(R_{M\alpha})} S_r^{R(B_\beta)} + \sum_{i,j} \langle 0 | E_{ij} | 0 \rangle \langle \varphi_{\perp \; i}^{(R_{M\alpha})} | \varphi_{\perp \; j}^{(B_\beta)} \rangle. \tag{61}$$

E. Gauge origin independence of calculated VCD

Consider a different gauge origin $\mathbf{O}_2$ displaced by a vector $\mathbf{V}$ from the original origin

$$\mathbf{O}_2 = \mathbf{O} + \mathbf{V}. \tag{62}$$

The polar tensors are independent of the magnetic field and therefore also independent of the gauge origin. The APTs calculated using the two origins are therefore equal

$$P_{M\alpha,\beta}^{(O_2)} = P_{M\alpha,\beta}^{(O)}. \tag{63}$$

In contrast, the axial tensors are known to be gauge origin dependent.[4] Since the densities, the $D_{ij}^{(R_{M\alpha})}$ elements, and the orbital and CSF response amplitudes in Eq. (61) are gauge independent for LAOs (Refs. 19, 22) the gauge dependence of $I_{M\alpha,\beta}$ results from the terms involving $D_{ij}^{(B_\beta)}$ and $\langle \varphi_{\perp \; i}^{(R_{M\alpha})} | \varphi_{\perp \; j}^{(B_\beta)} \rangle$. The origin dependence of these quantities arises from the factors

$$\mathbf{Q}^{M O_2} = \mathbf{Q}^{MO} - \mathbf{Q}^{O_2 O}. \tag{64}$$

The origin dependence of $D_{ij}^{(B_\beta)}$ and $\langle \varphi_{\perp \; i}^{(R_{M\alpha})} | \varphi_{\perp \; j}^{(B_\beta)} \rangle$ are found by inserting this expression into Eqs. (59) and (60),

$$D_{ji}^{(B_\beta)(O_2)} = D_{ji}^{(B_\beta)(O)} + \frac{i}{2} \mathbf{Q}_\beta^{O_2 O} \langle \psi_j | \mathbf{r} | \psi_i \rangle, \tag{65}$$

$$\langle \varphi_{\perp \; i}^{(R_{M\alpha})} | \varphi_{\perp \; j}^{(B_\beta)} \rangle^{(O_2)}$$

$$= \langle \varphi_{\perp \; i}^{(R_{M\alpha})} | \varphi_{\perp \; j}^{(B_\beta)} \rangle^{(O)} + \frac{i}{2} \mathbf{Q}_\beta^{O_2 O} \left\{ \left\langle \frac{\partial \psi_i}{\partial R_{M\alpha}} \middle| \mathbf{r} \middle| \psi_j \right\rangle \right.$$

$$\left. - \sum_{\rho\delta} \sum_k \left\langle \frac{\partial \psi_i}{\partial R_{M\alpha}} \middle| \psi_k \right\rangle \langle \psi_k | \mathbf{r} | \psi_j \rangle \right\}. \tag{66}$$

When these equations are inserted in Eq. (61) and Eq. (42) is used to simplify the expression, the origin dependence of $I_{M\alpha,\beta}$ is found as

$$I_{M\alpha,\beta}^{(O_2)} = I_{M\alpha,\beta}^{(O)} - \frac{i}{4} \mathbf{Q}_\beta^{O_2 O} \sum_{i,j,k,l} \kappa_{kl}^{I(R_{M\alpha})} \langle \psi_i | \mathbf{r} | \psi_j \rangle$$

$$\times \langle 0 | [E_{ij}, E_{kl}] | 0 \rangle - \frac{i}{4} \mathbf{Q}_\beta^{O_2 O} \sum_{i,j} \sum_r S_r^{I(R_{M\alpha})}$$

$$\times \langle \psi_i | \mathbf{r} | \psi_j \rangle \langle 0 | [E_{ij}, R_r^+] | 0 \rangle$$

$$+ \frac{i}{4} \mathbf{Q}_\beta^{O_2 O} \sum_{i,j} \left\{ \left[2 \left\langle \frac{\partial \psi_i}{\partial R_{M\alpha}} \middle| \mathbf{r} \middle| \psi_j \right\rangle \right. \right.$$

$$\left. \left. - \frac{\partial S_{ik}}{\partial R_{M\alpha}} \langle \psi_i | \mathbf{r} | \psi_j \rangle \right] \langle 0 | E_{ij} | 0 \rangle \right\}. \tag{67}$$

This equation may be simplified further by identifying on the right-hand side the first term in the APT as expressed in Eq. (52). The reduced equation reads

$$I_{M\alpha,\beta}^{(O_2)} = I_{M\alpha,\beta}^{(O)} - \frac{i}{4} \sum_{\gamma\delta} \epsilon_{\beta\gamma\delta} V_\gamma E_{M\alpha,\delta}, \tag{68}$$

where V_γ is the γth Cartesian coordinate of $\mathbf{V}$.

The origin dependence of the second contribution to AAT is evaluated as

$$J_{M\alpha,\beta}^{(O_2)} = J_{M\alpha,\beta}^{(O)} - \frac{i}{4} \sum_\gamma \epsilon_{\alpha\beta\gamma} V_\gamma Z_M$$

$$= J_{M\alpha,\beta}^{(O)} - \frac{i}{4} \sum_{\gamma\delta} \epsilon_{\beta\gamma\delta} V_\gamma N_{M\alpha,\delta} \tag{69}$$

and combining this equation with Eq. (68) we discover how the AAT depends on the gauge origin

$$M_{M\alpha,\beta}^{(O_2)} = M_{M\alpha,\beta}^{(O)} - \frac{i}{4} \sum_{\gamma\delta} \epsilon_{\beta\gamma\delta} V_\gamma P_{M\alpha,\delta}. \tag{70}$$

This is the same expression as for the exact wave function.[4] Equations (63) and (70) may now be used to relate the vibrational rotational strengths obtained with two different gauge origins $\mathbf{O}$ and $\mathbf{O}_2$,

$$R(0 \to 1)_n^{(O_2)} = R(0 \to 1)_n^{(O)} - \tfrac{1}{4} \tilde{\mathbf{P}}_n (\mathbf{V} \times \tilde{\mathbf{P}}_n)$$

$$= R(0 \to 1)_n^{(O)}. \tag{71}$$

Thus the use of LAO ensures that $R(0 \to 1)_n$ is gauge independent.

Stephens has previously shown that $R(0 \to 1)_n$ is origin independent for exact wave functions and for SCF or MCSCF calculations if complete basis sets are used.[4] In practice exact wave functions are not available and calculations are carried out with finite basis sets. If conventional orbitals are used the rotational strength is gauge origin dependent.[4,11] As shown above this deficiency is remedied when LAOs are used. Comparing Eqs. (63), (70), and (71) with exact theory, we see that finite basis set calculations with LAOs give an origin dependence of the AATs and an origin independence of the rotational strengths that fully correspond to the exact theory.

F. Gauge origin independence of VCD for other wave functions

The gauge origin independence of VCD found in the previous section for LAOs was derived for MCSCF wave

TABLE I. Basis sets and energies calculated for NH_3. N is the number of basis functions in each basis set. Energies in atomic units.

Label	Basis	N	SCF energy	CAS 1 energy
pVDZ	$(9s4p1d/4s1p)-[3s2p1d/2s1p]$	30	$-56.195\ 752$	$-56.300\ 382$
pVTZ(nf)	$(10s5p2d1f/5s2p1d)-[4s3p2d/3s2p]$	52	$-56.216\ 850$	$-56.325\ 071$
pVTZ	$(10s5p2d1f/5s2p1d)-[4s3p2d1f/3s2p1d]$	80	$-56.218\ 358$	$-56.326\ 704$
pVTZ(u)	$(10s5p2d1f/5s2p1d)-[5s4p2d1f/4s2p1d]$	87	$-56.218\ 581$	$-56.327\ 473$
pVTZ(uu)	$(10s5p2d1f/5s2p1d)-[6s5p2d1f/5s2p1d]$	94	$-56.218\ 602$	$-56.327\ 498$
pVTZ($+$)	$(11s6p2d1f/6s2p1d)-[5s4p2d1f/4s2p1d]$	87	$-56.220\ 174$	$-56.329\ 567$
pVTZ($++$)	$(12s7p3d1f/7s3p1d)-[6s5p3d1f/5s3p1d]$	109	$-56.220\ 477$	$-56.330\ 016$
pVTZ($+++$)	$(13s8p4d1f/8s4p1d)-[7s6p4d1f/6s4p1d]$	131	$-56.220\ 526$	$-56.330\ 072$
A105	$(13s8p4d1f/10s3p)-[8s6p4d1f/6s3p]$	105	$-56.224\ 039$	$-56.334\ 162$

functions. However, from our derivation it can be seen that the origin independence applies to any wave function spanned in a basis of LAOs.

The parametrization specifying the unitary transformation Eq. (23) refers to a MCSCF wave function. The parametrization of other wave functions such as configuration interaction (CI) or coupled cluster (CC) takes similar forms and the parameters in Eqs. (27), (44), (52), and (53) may be determined in the same way for such wave functions. The origin dependence of AATs arises from $D_{ij}^{(B\beta)}$ and $\langle \varphi_{\perp\,i}^{(R_{M\alpha})} | \varphi_{\perp\,j}^{(B\beta)} \rangle$ only. These terms depend on the basis set but not on the wave function. When LAOs are used, the gauge origin dependence of the AAT will have the form of Eq. (70) for any wave function. Therefore, the origin independence of vibrational rotational strengths based on Eq. (70) holds for any wave function spanned by a set of LAOs.

III. CALCULATIONS WITH RESULTS AND DISCUSSION

The theory presented above has been implemented in the ABACUS program.[23(a)] The implementation includes the analytical evaluation of response equations with respect to the magnetic field. The integrals required for the use of LAOs are evaluated using the McMurchie–Davidson scheme.[24] The wave function has been calculated using the SIRIUS program.[23(b)]

Using conventional AOs the VCD of the ammonia isotopomer NHDT has been investigated at the SCF level of approximation by Jalkanen and co-workers.[9,11–13,25] In particular the dependence on the basis set and the gauge origin has been examined. Results have been compared using analytical coupled Hartree–Fock theory and an approach where all matrix elements are obtained from RPA neglecting the geometry dependence of the basis set. In addition, the accuracy of the different representations of APTs has been analyzed. For calculations with conventional basis sets the conclusions are that the DO gauge with origins at the nuclei is to be preferred over the CO gauge, and that the length form is to be preferred for calculations of APTs.[13] As the geometry dependence of the basis set was neglected, the RPA results are competitive only when so-called polarized basis sets are used.[13,26]

In this work the atomic tensors for the ground electronic state of NH_3 ($^1A_1$) and the vibrational rotational strengths of NHDT have been calculated both at the SCF and the MCSCF level using conventional AOs and LAOs. The polar tensors are calculated in the length form and the CO gauge has been used for the axial tensors. The origin of the coordinate system is chosen as the center of mass of $^{14}NH_3$ at the experimental geometry ($r_{N-H} = 1.0116$ Å and $\theta_{HNH} = 106.7°$),[27] and the CO is taken to coincide with this origin. The Cartesian coordinates of N, H1, H2, and H3 in atomic units are $(0, 0, 0.1278)$, $(-0.885\ 5, 1.533\ 730\ 990\ 1, -0.592\ 0)$, $(-0.885\ 5, -1.533\ 730\ 990\ 1, -0.592\ 0)$, and $(1.771\ 0, 0, -0.592\ 0)$, respectively. We have used Dunning's correlation consistent pVDZ and pVTZ basis sets as our primary basis,[28] but have also carried out calculations with the largest basis from Ref. 13. The smallest pVDZ basis consists of 30 contracted functions (see Table I). Next follows the pVTZ(nf) basis set obtained from pVTZ by omitting the f function on N and the d function on H (52 contracted) and the pVTZ basis itself (80). The pVTZ(u) (87) and pVTZ(uu) (94) basis sets are obtained by uncontracting diffuse functions in pVTZ. The uncontracted functions in pVTZ(u) are the most diffuse s and p functions on N and the most diffuse s function on H. In pVTZ(uu) also the second outermost s and p functions on N and the second outermost s function on H are uncontracted. The pVTZ($+$) (87), pVTZ($++$) (109), and pVTZ($+++$) (131) basis sets are obtained by adding diffuse functions to pVTZ. For pVTZ($+$) the added functions are s ($\alpha = 0.0576$) and p ($\alpha = 0.0491$) on N and s ($\alpha = 0.025\ 26$) on H. For pVTZ($++$) the added functions are the same as for pVTZ($+$) plus s ($\alpha = 0.0192$), p ($\alpha = 0.016\ 37$), and d ($\alpha = 0.1563$) functions on N and s ($\alpha = 0.008\ 42$) and p ($\alpha = 0.129\ 33$) functions on H. Finally, pVTZ($+++$) is obtained from pVTZ($++$) by adding s ($\alpha = 0.0064$), p ($\alpha = 0.005\ 46$), and d ($\alpha = 0.0521$) functions on N, and s ($\alpha = 0.002\ 81$) and p ($\alpha = 0.043\ 11$) functions on H. The last A105 (105) basis is taken from Ref. 13 and is based on the orbital set of van Duijneveldt.[29]

The MCSCF wave functions for the correlated calculations are CAS wave functions. Two different CAS are employed. CAS1 contains 924 CSFs that result from distributing eight electrons in the eight active orbitals (2,4,0).
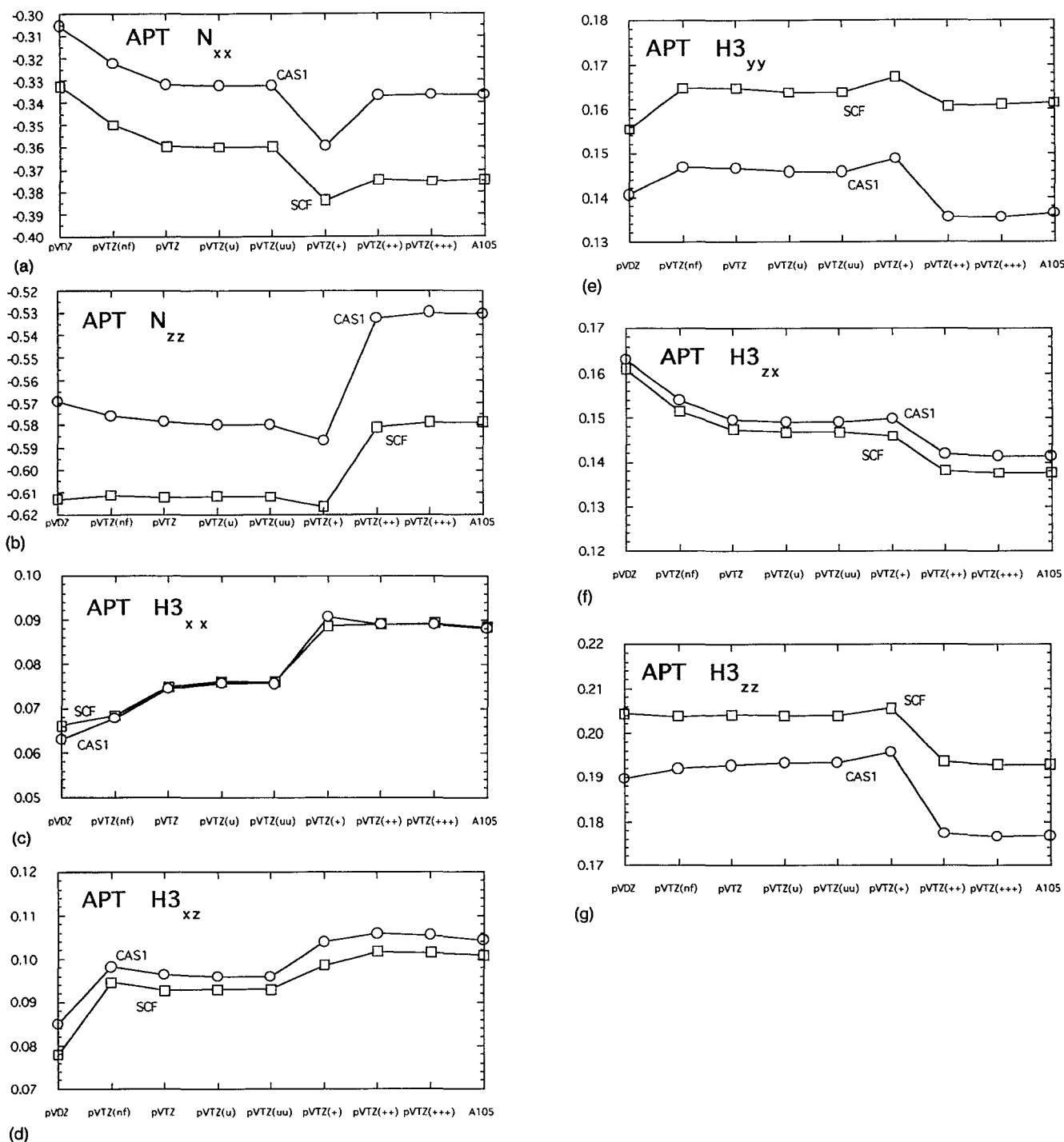
FIG. 1. The symmetry independent APT components obtained for NH_3 with different basis sets. Values in atomic units.

The numbers in parentheses give the number of active orbitals of symmetry e, a_1, and a_2, respectively. CAS2 is larger and contains the 71 947 CSFs obtained by distributing eight electrons in 13 active orbitals (4,5,0).

A. Basis set effects

The SCF and correlated CAS1 results obtained for the various basis sets are found in Figs. 1–5. Although SCF and CAS1 results differ significantly, they have the same dependence on the basis sets. In this section we therefore discuss the basis set effects without referring specifically to the uncorrelated or the correlated results.

The independent nonzero components of the atomic tensors for the various basis sets are found in Figs. 1(a)–1(g) (APTs) and Figs. 2(a)–2(e) (AATs). For easy comparison the vertical axes in each case span 0.05 a.u. However, Figs. 1(a) and 1(b) are exceptions and their vertical axes span 0.10 a.u. For polar tensors, the uncontraction of functions in pVTZ has little effect, but the components change significantly when going from pVDZ to pVTZ and when diffuse functions are added. The pVTZ($++$), pVTZ($+++$), and A105 basis sets give very similar results, and the APT has converged for pVTZ($++$).
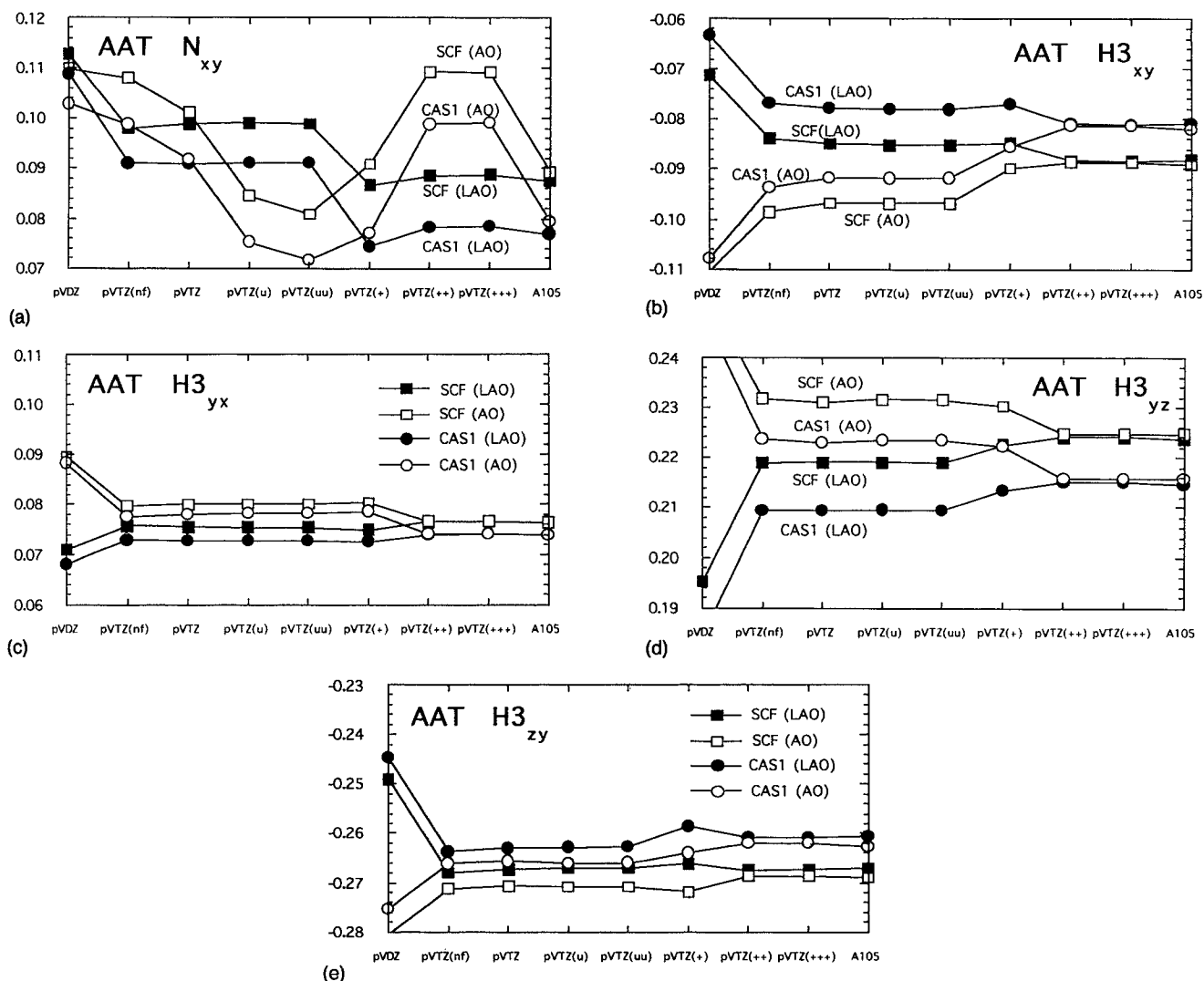
FIG. 2. The symmetry independent imaginary AAT components obtained for NH_3 with different basis sets. Results obtained from London atomic orbitals are marked with (LAO) and those obtained from conventional atomic orbitals are marked with (AO). Values in atomic units.

The axial tensors have been calculated with and without the use of LAOs, see Figs. 2(a)–2(e). When LAOs are used, the uncontraction of functions in pVTZ has no effect. Also, the components change significantly when going from pVDZ to pVTZ(nf) and when diffuse functions are added. The highest angular momentum polarization functions in pVTZ are unimportant and the effect of adding the second and third set of diffuse functions [going from pVTZ($+$) to pVTZ($++$) and to pVTZ($+++$)] is also small. Apparently, the axial tensors are converged for pVTZ($++$). As for the polar tensors, A105, pVTZ ($++$), pVTZ($+++$) give very similar results.

When conventional AOs are used, the N_{xy} axial component is erratic and differs substantially from the LAO calculations. For example, the results obtained with A105 and pVTZ($+++$) differ by as much as 0.02 a.u. The agreement with the LAO calculation for A105 may therefore be accidental. In contrast, the AAT components for hydrogen calculated from conventional basis sets are similar to those obtained using LAOs. The uncontraction of functions in pVTZ has little effect, but significant changes

are observed when going from pVDZ to pVTZ(nf) and when diffuse functions are added. The components converge from above without London orbitals and from below when the London orbitals are used. The fact that pVTZ ($++$) gives identical results with and without London orbitals indicates that these components are converged.

Stephens *et al.*[13] have shown that for neutral systems the following four tensors defined as sums over atomic tensors and dipole components are of interest,

$$\overset{0}{\underset{\alpha\beta}{\sum}} = \sum_M P_{M\alpha,\beta}, \quad \overset{1}{\underset{\alpha\beta}{\sum}} = \sum_\gamma \epsilon_{\alpha\beta\gamma}(\mu_{\text{el}})^0_\gamma, \tag{72a}$$

$$\overset{2}{\underset{\alpha\beta}{\sum}} = \sum_{M\gamma\delta} \epsilon_{\beta\gamma\delta} R_{0M\gamma} P_{M\delta,\alpha}, \quad \overset{3}{\underset{\alpha\beta}{\sum}} = 4 \sum_M \text{Im}[M_{M\alpha,\beta}]. \tag{72b}$$

Here $(\mu_{\text{el}})^0_\gamma$ denotes the γth component of the electric dipole moment at the equilibrium geometry $\mathbf{R}_0$. For exact wave functions and in the Hartree–Fock limit these tensors obey the following sum-rules:[13]
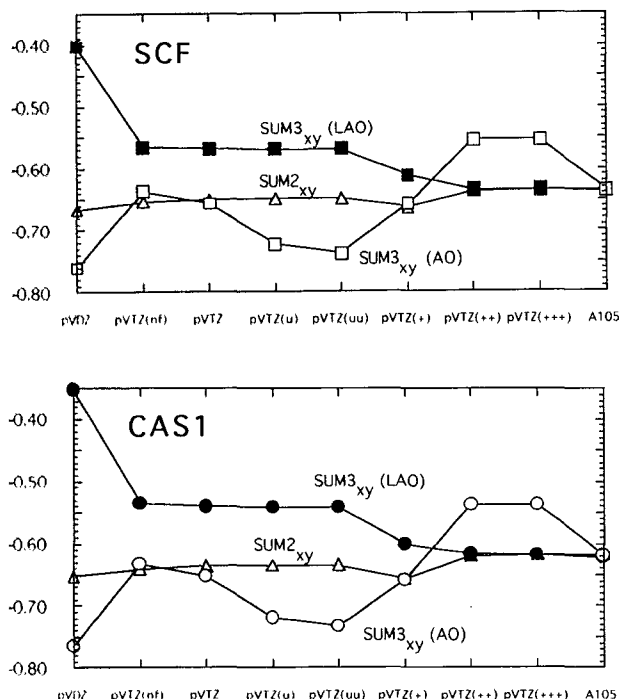
FIG. 3. Σ_{xy}^2 and Σ_{xy}^3 obtained at the SCF and CAS1 levels for NH_3 for various basis sets. Results obtained from London atomic orbitals are marked with (LAO) and results obtained from conventional atomic orbitals are marked with (AO). Values in atomic units.

$$\sum_{\alpha\beta}^{0} = 0, \quad \sum_{\alpha\beta}^{1} = \sum_{\alpha\beta}^{2} = \sum_{\alpha\beta}^{3}. \tag{73}$$

In fact, the $\Sigma_{\alpha\beta}^0=0$ and $\Sigma_{\alpha\beta}^1=\Sigma_{\alpha\beta}^2$ rules hold for any basis set when the polar tensors are calculated in the length form. In this context, the only rule of interest is $\Sigma_{\alpha\beta}^2=\Sigma_{\alpha\beta}^3$. In our calculations, the only nonzero sums are $\Sigma_{xy}= -\Sigma_{yx}$. In Figs. 3(a) and 3(b) we have plotted Σ_{xy}^2 and Σ_{xy}^3 as functions of basis sets. The polar sum Σ_{xy}^2 changes only slightly as the basis set is increased. The axial sums Σ_{xy}^3 are calculated using conventional and London orbitals. The behavior of the Σ_{xy}^3 sums reflects the behavior of the corresponding N_{xy} AAT components. While Σ_{xy}^3 calculated from conventional basis sets does not converge, Σ_{xy}^3 calculated using the London basis sets converges, and for LAOs the differences between Σ_{xy}^2 and Σ_{xy}^3 are practically zero for pVTZ($++$), pVTZ($+++$), and A105.

The Cartesian to normal coordinate transformation matrix is determined for the chiral system NHDT from the calculated molecular gradient and Hessian for each basis set. The six fundamental harmonic frequencies corresponding to the normal coordinates are shown in Figs. 4(a)–4(f). The frequencies change dramatically when going from pVDZ to pVTZ(nf). Further extensions of the basis hardly change the frequencies.

From the atomic tensors and normal coordinates we calculate the vibrational rotational strengths using Eqs. (4) and (5), see Figs. 5(a)–5(f). The first three [Figs. 5(a)–5(c)] correspond to the higher frequencies and behave in the same way. In particular, the results obtained from conventional and London basis sets differ only

slightly. They change significantly from pVDZ to pVTZ and also when diffuse functions are added to the pVTZ basis.

The vibrational rotational strengths corresponding to the three lower frequencies [Figs. 5(d)–5(f)] are an order of magnitude larger than those of the higher frequencies. Here the difference between strengths obtained from conventional and London basis sets are large for the small and medium sized basis sets. For the three largest basis sets the rotational strengths calculated with and without the use of LAOs agree. The rotational strengths change significantly when going from pVDZ to pVTZ(nf). Adding polarization functions and uncontracting functions have little effect, but particularly the strengths calculated from conventional basis sets change when extra diffuse functions are added. The results obtained from the three largest basis sets agree and thus the rotational strengths are nearly converged for the pVTZ($++$) basis. Clearly, the vibrational rotational strengths obtained with LAOs are significantly better than those obtained from conventional AOs when the medium sized basis sets are used, and we expect this effect to be more pronounced for larger molecules where there is no natural choice of the common gauge origin.

B. Correlation effects

The basis set analysis indicates that the LAO pVTZ ($++$) basis is adequate for describing the VCD of NHDT. The LAO pVTZ($++$) basis has therefore been used for the SCF, CAS1, and CAS2 calculations in Table II.

The largest correlation effect for the polar tensor is found for the N_{zz} component and it amounts to 0.049 (8.4%) and 0.038 (6.6%) a.u. at the CAS1 and CAS2 levels. The range of correlation for the polar tensor is 0 to 16% at the CAS1 level and only 0 to 9% at the CAS2 level. For the axial tensor the largest correlation effect amounts to 0.010 a.u. for the N_{xy} component at the CAS1 level. This corresponds to 11.7% and is the largest correlation effect for the axial tensor. However, at the CAS2 level the correlation for the N_{xy} component has dropped to 1.9% and the largest correlation is found for the $H3_{xy}$ component (0.005 a.u. or 5.7%). Thus, the AAT correlation effects are small but not negligible.

The effect of correlation on the three highest frequencies is <1% for CAS1. CAS2 modifies the CAS1 results only slightly such that the largest correlation effect becomes 1.2%. In wave numbers, the largest correlation for the three highest frequencies is 38 cm^{-1} calculated for frequency one at the CAS2 level. Correlation is more important for the three lowest frequencies where it contributes from 7% to 14% to the frequencies regardless of correlation level. The largest correlation is found for the lowest frequency and is 135 and 133 cm^{-1} at the CAS1 and CAS2 levels. Again CAS2 modifies the CAS1 correlation only slightly.
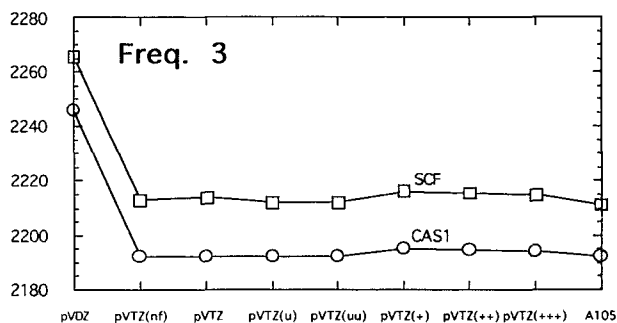
The correlation effects are significant for the vibrational rotational strengths. The largest correlations, found for the fifth rotational strength, are respectively, 2.4 (20%) and 1.7×10^{-44} esu^{-2} cm^{-2} (14%) at the CAS1
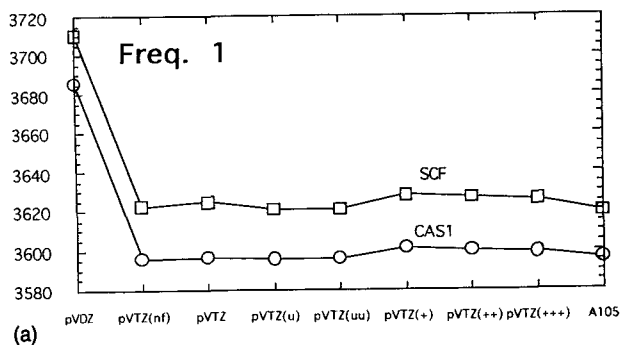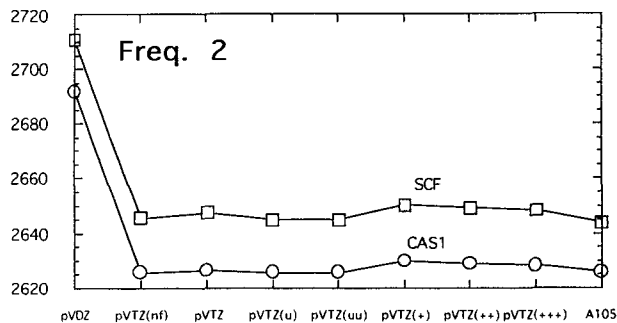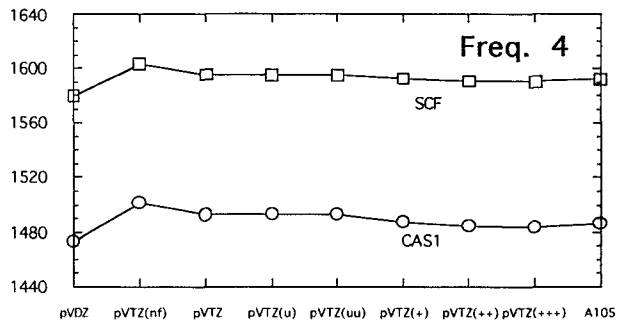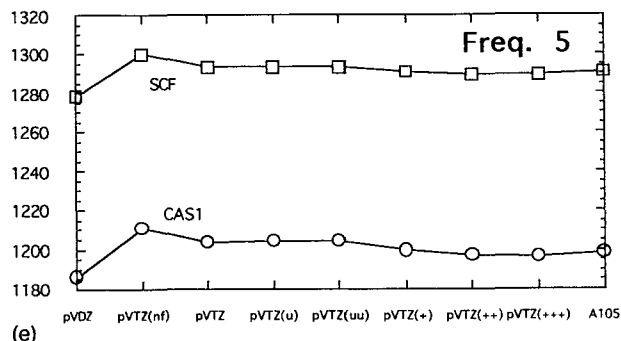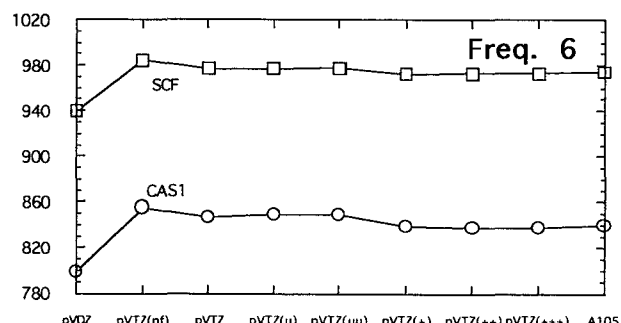
FIG. 4. Normal frequencies obtained for NHDT for various basis sets. Values in cm^{-1}.

and CAS2 levels. However, the relative effects are 25% for the sixth strength at the CAS1 level and 31% for the first strength at the CAS2 level. As for the atomic tensors, the correlations found at the CAS1 and CAS2 levels fluctuate considerably for the vibrational rotational strengths and further calculations are required to establish the correlation limit.

IV. SUMMARY AND CONCLUDING REMARKS

We have derived general expressions for the calculation of MCSCF wave functions differentiated with respect to an arbitrary parameter. Identifying this parameter with the nuclear coordinates and the components of the mag-

netic field, we have determined the atomic polar and axial tensors. These expressions are used in Stephens' equation to determine the vibrational rotational strengths and the VCD spectrum.

Using London atomic orbitals, we have obtained vibrational rotational strengths that are gauge independent in the same manner as for exact wave functions; the AAT depends on the gauge but the rotational strength is independent. LAOs therefore are extremely useful in calculations of VCD as they are for other magnetic properties such as nuclear magnetic shieldings and magnetizabilities.

SCF and MCSCF calculations on NH$_3$ and its isotopomer NHDT are presented. Basis set analyses show
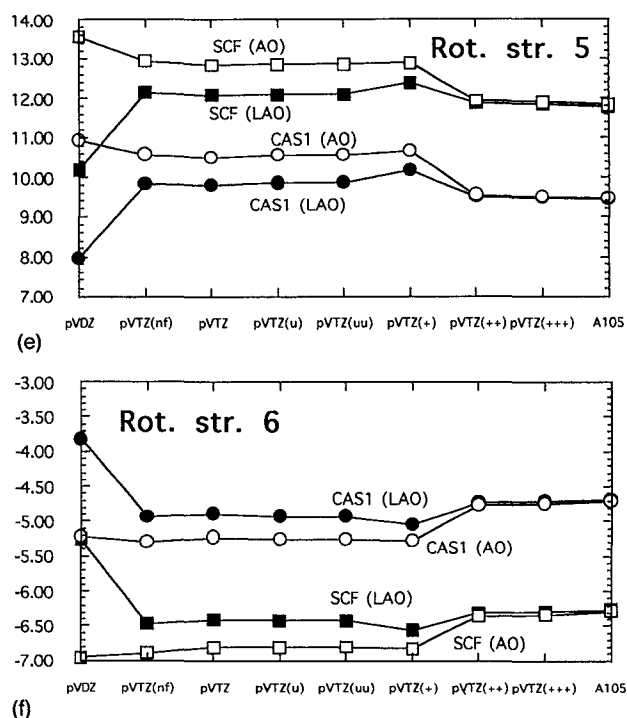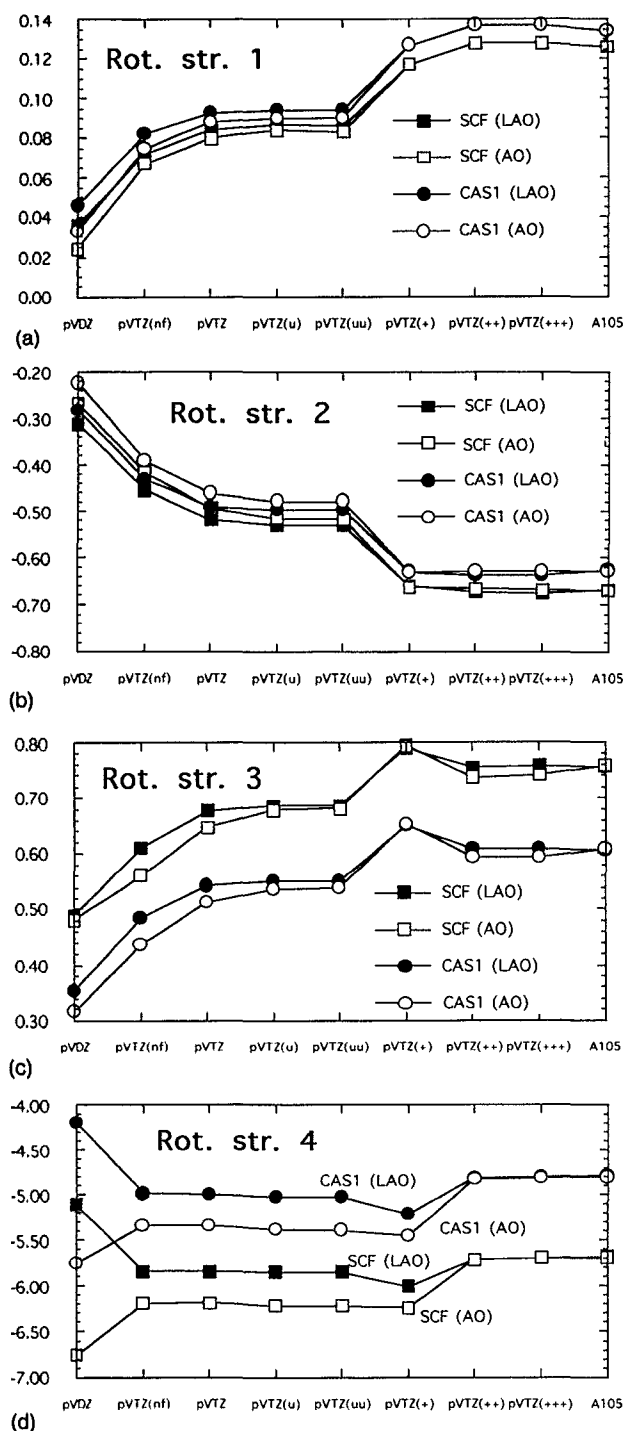
FIG. 5. Vibrational rotational strengths obtained for NHDT for various basis sets. Results obtained from London atomic orbitals are marked with (LAO) and results obtained from conventional orbitals are marked with (AO). Values in 10^{-44} esu^2 cm^2.

that in addition to making the vibrational rotational strengths origin independent, LAOs also give better convergence of the atomic axial tensors and the vibrational rotational strengths. Basis sets of pVTZ quality are needed for the reliable calculation of atomic tensors, and for quantitative results one set of diffuse functions must be added. With the use of LAOs the calculated axial tensors converge as fast as if not faster than the polar tensors. This implies that the calculation of vibrational rotational strengths is not more difficult than the calculation of vibrational intensities.

The MCSCF wave functions are taken as CAS wave functions and two levels of correlation (CAS1 and CAS2)

are used for the calculations. AATs are here reported at a correlated level for the first time. The observed correlation effects are of the same magnitude for the AATs as for APTs and in the range from 0 to 15%. The correlation effects calculated for the vibrational rotational strengths range from 0 to 30%.

The London approach introduces atomic integrals involving integration over complex phase factors. The London method therefore involves more extensive coding. However, comparison of the timings for the SCF and MCSCF LAO and corresponding AO calculations shows that the overhead as a result of using LAOs is small (<30%). The London method thus appears to be the

TABLE II. Electronic energies, atomic tensors, frequencies, and vibrational rotational strengths calculated from the LAO pVTZ($++$) basis set. The imaginary part of the purely imaginary atomic axial tensor is listed. All values in atomic units except frequencies (cm^{-1}) and vibrational rotational strengths (10^{-44} esu^2 cm^2).

		SCF	CAS1	CAS2
Energy		$-56.220\,477$	$-56.330\,016$	$-56.401\,063$
APT	N_{xx}	-0.375	-0.337	-0.374
	N_{zz}	-0.581	-0.532	-0.543
	$H3_{xx}$	0.089	0.089	0.097
	$H3_{xz}$	0.102	0.106	0.109
	$H3_{yy}$	0.161	0.135	0.152
	$H3_{zx}$	0.138	0.142	0.131
	$H3_{zz}$	0.194	0.177	0.181
AAT	N_{xy}	0.089	0.078	0.087
	$H3_{xy}$	-0.088	-0.081	-0.083
	$H3_{yx}$	0.077	0.074	0.077
	$H3_{yz}$	0.224	0.215	0.227
	$H3_{zy}$	-0.267	-0.261	-0.269
Freq.	1	3627	3600	3589
	2	2649	2629	2622
	3	2215	2195	2188
	4	1591	1484	1473
	5	1289	1197	1188
	6	973	837	840
Rot. str.	1	0.128	0.137	0.168
	2	-0.673	-0.635	-0.787
	3	0.754	0.608	0.755
	4	-5.710	-4.818	-5.143
	5	11.881	9.504	10.185
	6	-6.305	-4.724	-5.108

method of choice for calculations involving an external magnetic field. Calculations of rotational strength on systems with large static correlation would be interesting and are currently under way.

ACKNOWLEDGMENTS

APPENDIX

The Hamiltonian operator for a one-electron, one-center problem in presence of an external magnetic field reads

$$H = \tfrac{1}{2}(-i\nabla + \mathbf{A})^2 - \frac{Z_N}{|\mathbf{r} - \mathbf{R}_N|}, \qquad (A1)$$

where Z_N and $\mathbf{R}_N$ are the charge and the position of the center which is thought of as a fixed nucleus. The $\mathbf{r}$ is the position of the electron and $\mathbf{A}$ is the magnetic vector potential defined as

$$\mathbf{A} = \tfrac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O}) \qquad (A2)$$

with $\mathbf{B}$ denoting the external magnetic field and $\mathbf{O}$ being the gauge origin.

The magnetic vector potential vanishes if the magnetic field is zero, and in this case we denote the Hamiltonian H_0. The atomic orbitals (AOs) which are eigenfunctions for H_0,

$$H_0 \chi_{nlm} = E_n \chi_{nlm} \qquad (A3)$$

are characterized by the principal quantum number n, and the angular momentum quantum numbers l and m. LAOs are formed by multiplying the AOs with a phase factor

$$\omega_{nlm} \equiv \exp(-i\mathbf{A}_N^e \cdot \mathbf{r})\chi_{nlm}, \qquad (A4)$$

where

$$\mathbf{A}_N^e = \tfrac{1}{2}\mathbf{B} \times (\mathbf{R}_N - \mathbf{O}). \qquad (A5)$$

Operating on a LAO with the Hamiltonian gives

$$H\omega_{nlm} = \exp(-i\mathbf{A}_N^e \cdot \mathbf{r})\left\{ \tfrac{1}{2}[-i\nabla + (\mathbf{A} - \mathbf{A}_N^e)]^2 \right.$$

$$\left. - \frac{Z_N}{|\mathbf{r} - \mathbf{R}_N|}\right\} \chi_{nlm}. \qquad (A6)$$

Denoting the z component of the electronic angular momentum operator with l_z and assuming that the $\mathbf{B}$ field lies along the z-axis, this expression can be rewritten by expanding the operator on the right-hand side in orders of $\mathbf{B}$,

$$H\omega_{nlm} = \exp(-i\mathbf{A}_N^e \cdot \mathbf{r})(H_0 + \tfrac{1}{2}B_z l_z)\chi_{nlm} + O^2(\mathbf{B})$$

$$= \omega_{nlm}(E_n + \tfrac{1}{2}B_z m) + O^2(\mathbf{B}). \qquad (A7)$$

For the one-electron, one-center problem it is thus shown that the LAOs, formed from AO eigenfunctions of the field free problem, are eigenfunctions to first order in $\mathbf{B}$.

Note, if the gauge origin of the vector potential is taken to be the center of the one-electron system, then the phase factor of the LAO is one and the AO by itself satisfy Eq. (A7). Importantly however, if the gauge origin is chosen to be different from the center of the system the AO unlike the LAO will not be an eigenfunction through first order and thus *not* fulfill Eq. (A7).

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