Static and frequency-dependent polarizabilities of excited singlet states using coupled cluster response theory

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We report an implementation of the linear response function for singlet excited states for the coupled cluster models CCS, CC2 and CCSD. The implementation is based on the derivation of excited state response functions as derivatives of excited state quasienergy Lagrangians. Secular divergencies are explicitly eliminated and response equations and response functions therefore are numerical stable in the static limit. Calculations are performed for the polarizabilities of pyrimidine and *s*-tetrazine in their lowest singlet excited states. We find that the results for the excited state polarizabilities are sensitive to the accuracy of the excitation energies and that a qualitative correct description of the dispersion is first obtained at a correlated level. © *1998 American Institute of Physics.* [S0021-9606(98)31244-1]

I. INTRODUCTION

Static and frequency-dependent polarizabilities of excited states are key quantities in the understanding and description of a number of experimental phenomena including, for example, the Stark effect, electrochromic properties and solvatochromatic shifts of excitation energies. While the experimental determination of electro- and solvatochromic properties refers to measurements in solution[1–4] and can therefore not be compared directly with single molecule *ab initio* calculations, laser Stark spectroscopy measurements are directly related to (excited state) properties of isolated molecules as they are performed in the gas phase.[5–8] In recent years, experimental results for excited state polarizabilities and other excited state molecular properties have become increasingly more abundant in the literature.[1–4,6–9] In some cases it was, however, not possible to determine all components of the excited state polarizability tensors, and the assignment of the tensor components has often been difficult without additional information from calculations.[6,10]

The *ab initio* calculation of excited state polarizabilities is also a difficult task. It requires a method capable of predicting accurate excitation energies. Static polarizabilities of excited states can be calculated by combining such methods with a numerical differentiation (finite field) technique. Finite field calculations of static excited state polarizabilities have, for example, been carried out for the S_1 ($1\,^1B_{3u}$) state of *s*-tetrazine by Schütz *et al.*[10] employing the CASPT2 method and by Stanton and Gauss[11] using the coupled cluster singles and doubles (CCSD) model. Frequency-dependent excited state polarizabilities have been calculated, for example, by Pipin and Bishop[12] for Li in the $2\,^2P_{1/2}$ state employing a sum-over-state approach and wave functions obtained by a combined configuration-interaction-Hylleraas method. However, sum-over-state approaches are only applicable for few-electron systems or for semi-empirical wave functions and the finite field technique can only be used to calculate static polarizabilities. A more general and efficient approach is offered by the concept of analytic response functions.

In response theory, excited state polarizabilities can be obtained in two different ways: either by an explicit optimization of the excited state wave function combined with a linear response calculation or as the second-residue of the cubic response function of the ground state. These two approaches are only equivalent for a linear parametrization of the wave function, as used in configuration interaction (CI) based methods. For nonlinear parametrizations as in self-consistent-field (SCF), multiconfigurational self-consistent-field (MCSCF) or coupled cluster response theory, the two approaches lead in general to different results. The apparent advantage of calculating excited state polarizabilities as second-residues of the ground state cubic response function is that this does not require a nonlinear optimization of an excited state wave function. This approach is therefore applicable to a wider range of *ab initio* methods, including SCF and coupled cluster theory, where excited state optimizations cannot easily be performed. An implementation of excited state polarizabilities as second-residues of the ground state cubic response function was recently reported by Norman *et al.* for SCF[13] and by Jonsson *et al.* for MCSCF[14] wave functions. For CCSD wave functions excited state first-order properties were derived by Koch and Jørgensen[15] and by Stanton and Gauss,[16–18] who also discussed the theory for static excited state second-order properties.[19]

In the present publication we report an implementation of coupled cluster response theory[15,20–23] for static and frequency-dependent polarizabilities of excited states for the coupled cluster models CCS, CC2 and CCSD. The implementation is based on a Lagrangian for the excited state,[21,23,24] leading to excited state response functions which are equivalent to those identified from the double residues of the ground state response functions but with the artificial secular divergent terms removed.[23] Thereby the response

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equations and the expressions for the response functions remain numerical stable in the limit of static external fields. Applications of the implemented approach are presented for the dipole polarizabilities of the S_1 ($1\,^1B_{3u}$) state of *s*-tetrazine and the S_1 ($1\,^1B_1$) state of pyrimidine.

II. THEORY

In Ref. 23 we showed that in coupled cluster response theory the difference between the response functions of the excited state f and the ground state can be calculated as derivatives of the real part of the quasienergy difference between the two states:

$$\langle\langle X_1;\ X_2,\ldots,X_n\rangle\rangle^{(f)}_{\omega_2,\ldots,\omega_n}-\langle\langle X_1;\ X_2,\ldots,X_n\rangle\rangle^{(0)}_{\omega_2,\ldots,\omega_n}$$
$$=\left(\frac{d^n\{\frac{1}{2}\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)+\frac{1}{2}\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)^*\}_T}{d\epsilon_1(\omega_1)d\epsilon_2(\omega_2)\ldots d\epsilon_n(\omega_n)}\right)_0. \tag{1}$$

In Eq. (1) the derivatives are taken with respect to the field strengths of the external perturbation:

$$\hat{V}(t,\epsilon)=\sum_j \hat{H}^{X_j}\epsilon_j(\omega_j)e^{-i\omega_j t}, \tag{2}$$

$$\hat{H}(t,\epsilon)=\hat{H}^{(0)}+\hat{V}(t,\epsilon), \tag{3}$$

and the lower index 0 indicates that the derivative is taken for the zero field strength limit, i.e., for the unperturbed molecule. With $\{\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)\}_T$ we denote the quasienergy difference between state f and the ground state, defined as

$$\{\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)\}_T=\lim_{t_0\to\infty}\frac{1}{2t_0}\int_{-t_0}^{+t_0}\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)\,dt, \tag{4}$$

$$\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)=\left(\tilde{\bar{E}}^f(t,\epsilon)\left[\boldsymbol{A}(t,\epsilon)-i\frac{d}{dt}\right]\tilde{E}^f(t,\epsilon)\right)\times(\tilde{\bar{E}}^f(t,\epsilon)\tilde{E}^f(t,\epsilon))^{-1}. \tag{5}$$

The matrix $\boldsymbol{A}(t,\epsilon)$ is the field- and time-dependent coupled cluster Jacobian defined[22,23] as derivative of the time-dependent cluster equations with respect to the cluster amplitudes. Denoting the cluster equations in a shorthand form as $e_\mu(t,\epsilon)=i(d/dt)t_\mu(t,\epsilon)$, where $t_\mu(t,\epsilon)$ are the cluster amplitudes, the matrix $\boldsymbol{A}(t,\epsilon)$ is defined as the derivative:

$$A_{\mu\nu}(t,\epsilon)=\frac{de_\mu(t,\epsilon)}{dt_\nu}. \tag{6}$$

The vectors $\tilde{\bar{E}}^f(t,\epsilon)$ and $\tilde{E}^f(t,\epsilon)$ represent, respectively, the *phase-isolated* bra and ket wave functions of the excited state f in the biorthogonal basis spanned by the coupled cluster left projection manifold and the singles, doubles, etc. excitations out of the coupled cluster ground state wave function.[23] In the presence of a (quasi-)periodic perturbation as considered in Eq. (2), $\tilde{\bar{E}}^f(t,\epsilon)$ and $\tilde{E}^f(t,\epsilon)$ can be expanded in the field strengths of the perturbations as:[23]

$$\tilde{E}^f(t,\epsilon)=E^f(\omega_f)+\sum_{n=1}^{\infty}\frac{1}{n!}\sum_{j_1}\ldots\sum_{j_n}\tilde{E}^{fX_{j_1}\ldots X_{j_n}}(\omega_f,\omega_{j_1},\ldots,\omega_{j_n})\times\prod_{m=1}^{n}\epsilon_{j_m}(\omega_{j_m})e^{-i\omega_{j_m}t}, \tag{7}$$

$$\tilde{\bar{E}}^f(t,\epsilon)=\bar{E}^f(-\omega_f)+\sum_{n=1}^{\infty}\frac{1}{n!}\sum_{j_1}\ldots\sum_{j_n}\tilde{\bar{E}}^{fX_{j_1}\ldots X_{j_n}}(-\omega_f,\omega_{j_1},\ldots,\omega_{j_n})\times\prod_{m=1}^{n}\epsilon_{j_m}(\omega_{j_m})e^{-i\omega_{j_m}t}. \tag{8}$$

The time-evolution of the excited state vectors $\tilde{E}^f(t,\epsilon)$ and $\tilde{\bar{E}}^f(t,\epsilon)$ can be determined up to a normalization and a phase factor from a generalized Frenkel variation principle or by requiring $\{\Delta\dot{\mathscr{W}}_{0f}\}_T$ to be stationary.[23] The normalization and the phase of $\tilde{\bar{E}}^f(t,\epsilon)$ and $\tilde{E}^f(t,\epsilon)$ are determined by the conditions:

$$\tilde{\bar{E}}^f(t,\epsilon)\tilde{E}^f(t,\epsilon)=1, \tag{9}$$

$$\tilde{\bar{E}}^f(t,\epsilon)E^f(\omega_f)=\bar{E}^f(-\omega_f)\tilde{E}^f(t,\epsilon). \tag{10}$$

Inserting expansions (7) and (8) into Eqs. (9) and (10), the latter two equations can be combined to:

$$\begin{aligned}\bar{E}^f(\omega_f)\tilde{E}^{fX_1\ldots X_n}(\omega_f,\omega_1,\ldots,\omega_n)&=\tilde{\bar{E}}^{fX_1\ldots X_n}(-\omega_f,\omega_1,\ldots,\omega_n)E^f(\omega_f)\\&=\frac{1}{2}\hat{P}^{X_1\ldots X_n}\sum_{k=1}^{n-1}\tilde{\bar{E}}^{fX_1\ldots X_k}(-\omega_f,\omega_1,\ldots,\omega_k)\times\tilde{E}^{fX_{k+1}\ldots X_n}(-\omega_f,\omega_{k+1},\ldots,\omega_n).\end{aligned} \tag{11}$$

Thus the independent variables of the expansions in (7) and (8) are the coefficients of the projections of the excited state responses onto the orthogonal complement of the state f:

$${}^{\perp}\tilde{E}^{fX_1\ldots X_n}(\omega_f,\omega_1,\ldots,\omega_n)=\boldsymbol{Q}^f\tilde{E}^{fX_1\ldots X_n}(\omega_f,\omega_1,\ldots,\omega_n), \tag{12}$$

$${}^{\perp}\tilde{\bar{E}}^{fX_1\ldots X_n}(-\omega_f,\omega_1,\ldots,\omega_n)=\tilde{\bar{E}}^{fX_1\ldots X_n}(-\omega_f,\omega_1,\ldots,\omega_n)\boldsymbol{Q}^f, \tag{13}$$

where the projection operator $\boldsymbol{Q}^f$ is defined as:

$$Q^f_{\mu\nu}=\delta_{\mu\nu}-E^f_\mu(\omega_f)\bar{E}^f_\nu(-\omega_f). \tag{14}$$

To obtain efficient expressions for the calculation of the excited state response functions as derivatives of $\{\Delta\dot{\mathscr{W}}_{0f}\}_T$, we combine Eqs. (4) and (5) with the time-dependent ground state cluster equations to a *quasienergy difference* Lagrangian:

$$\Delta L^f(t,\epsilon)=\Delta\mathscr{W}_{0f}+\sum_\mu \tilde{\bar{N}}^f_\mu(t,\epsilon)\left(e_\mu(t,\epsilon)-i\frac{d}{dt}t_\mu(t,\epsilon)\right), \tag{15}$$

$$\{\Delta L^f(t,\epsilon)\}_T=\lim_{t_0\to\infty}\frac{1}{2t_0}\int_{-t_0}^{+t_0}\Delta L^f(t,\epsilon)dt. \tag{16}$$

The time-average $\{\Delta L^f\}_T$ can now be required to be stationary with respect to all its independent variables, i.e., the components of $\overline{E^f}(-\omega_f)$, $E^f(\omega_f)$, ${}^\perp\tilde{\bar{E}}^{fX_1\ldots X_n}(-\omega_f,\omega_1,\ldots,\omega_n)$, and ${}^\perp\tilde{E}^{fX_1\ldots X_n}(\omega_f,\omega_1,\ldots,\omega_n)$, as well as the ground state cluster amplitudes $t(t,\epsilon)$ and the excited state Lagrangian multipliers $\tilde{\bar{N}}^f(t,\epsilon)$:

$$\delta\{\Delta L^f(t,\epsilon)\}_T=0. \tag{17}$$

From the variational Lagrangian $\{\Delta L^f(t,\epsilon)\}_T$ the excited state quasienergy derivatives can be evaluated employing the $2n+1$ and $2n+2$ rules of variational perturbation theory[25–27,21] in order to minimize the maximum order of the response equations that have to be solved. To facilitate the calculations of derivatives of $\{\Delta L^f(t,\epsilon)\}_T$ with respect to the field strengths we introduce for the time-dependent cluster amplitudes the expansion:

$$t(t,\epsilon)=\sum_{n=0}^{\infty}\frac{1}{n!}\sum_{j_1}\cdots\sum_{j_n}t^{X_{j_1}\ldots X_{j_n}}(\omega_{j_1},\ldots,\omega_{j_n})\times\prod_{m=1}^{n}\epsilon_{j_m}(\omega_{j_m})e^{-i\omega_{j_m}t}, \tag{18}$$

and similar expansions for $\tilde{\bar{N}}^f(t,\epsilon)$ and $\Delta\mathscr{W}_{0f}(t,\epsilon)$. The expression for the difference between the linear response function of an excited state f and the ground state response function is in accordance with a $2n+1$ rule for $t(t,\epsilon)$ and $\tilde{E}^f(t,\epsilon)$ and a $2n+2$ rule for $\tilde{\bar{E}}^f(t,\epsilon)$ and $\tilde{\bar{N}}^f(t,\epsilon)$ found as:[23]

$$\begin{aligned}\langle\langle A;B\rangle\rangle^{(f)}_{\omega_B}-\langle\langle A;B\rangle\rangle^{(0)}_{\omega_B}&=\tfrac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{AB}\{\overline{E^f}(-\omega_f)(\boldsymbol{B}t^B(\omega_B)+\boldsymbol{A}^B)\tilde{E}^{fA}(\omega_f,\omega_A)\\&+\overline{E^f}(-\omega_f)(\tfrac{1}{2}\boldsymbol{C}t^A(\omega_A)t^B(\omega_B)+\boldsymbol{B}^At^B(\omega_B))E^f(\omega_f)\\&+\tilde{\bar{N}}^f(\tfrac{1}{2}\boldsymbol{B}t^A(\omega_A)t^B(\omega_B)+\boldsymbol{A}^At^B(\omega_B))\},\end{aligned} \tag{19}$$

with $\omega_A=-\omega_B$. The operator $\hat{C}^{\pm\omega}$ enforces symmetrization of the response function with respect to complex conjugation together with a simultaneous sign reversal of the frequencies ω_A, ω_B and implements a practical way of taking the derivative of the real part of the quasienergy difference Lagrangian. The matrices $\boldsymbol{A}^X$, $\boldsymbol{B}$, $\boldsymbol{B}^X$ and $\boldsymbol{C}$ are defined as partial derivatives of the Jacobian $\boldsymbol{A}(t,\epsilon)$:[22,23]

$$A^X_{\mu\nu}=\left(\frac{\partial A_{\mu\nu}(t,\epsilon)}{\partial\epsilon_X(0)}\right)_0, \tag{20}$$

$$B_{\gamma\mu\nu}=\left(\frac{\partial A_{\mu\nu}(t,\epsilon)}{\partial t_\gamma}\right)_0, \tag{21}$$

$$B^X_{\gamma\mu\nu}=\left(\frac{\partial^2 A_{\mu\nu}(t,\epsilon)}{\partial\epsilon_X(0)\partial t_\gamma}\right)_0, \tag{22}$$

$$C_{\eta\gamma\mu\nu}=\left(\frac{\partial^2 A_{\mu\nu}(t,\epsilon)}{\partial t_\eta\partial t_\gamma}\right)_0. \tag{23}$$

The stationarity conditions for $\{\Delta L^f\}_T$ with respects to variations of the independent variables of $\tilde{\bar{E}}^f(t,\epsilon)$ and $\tilde{E}^f(t,\epsilon)$ lead to the same equations as the stationarity conditions for $\{\Delta\mathscr{W}_{0f}\}_T$, which give in zeroth-order the eigenvalue equations

$$(\boldsymbol{A}-\omega_f\boldsymbol{1})E^f(\omega_f)=0, \tag{24}$$

$$\overline{E^f}(-\omega_f)(\boldsymbol{A}-\omega_f\boldsymbol{1})=0, \tag{25}$$

and for the first-order response of the right excited state vectors the response equation:

$$\begin{aligned}&(\boldsymbol{A}-(\omega_f+\omega_A)\boldsymbol{1})\,{}^\perp\tilde{E}^{fA}(\omega_f,\omega_A)\\&\quad=-\boldsymbol{Q}^f(\boldsymbol{B}t^A(\omega_A)+\boldsymbol{A}^A)\tilde{E}^f(\omega_f).\end{aligned} \tag{26}$$

The reference state component of $\tilde{E}^{fA}(\omega_f,\omega_A)$ is found from Eq. (11) as

$$\overline{E^f}(-\omega_f)\tilde{E}^{fA}(\omega_f,\omega_A)=0. \tag{27}$$

The $\boldsymbol{A}$ matrix occurring in the above equations is the standard time- and field-independent coupled cluster Jacobian. Since Eq. (26) is projected to the orthogonal complement of f, the first-order response of the excited state $\tilde{E}^{fA}(\omega_f,\omega_A)$ remains well-defined and finite in the static limit $\omega_A\to 0$, as long as the state f is not degenerated. This is in contrast to the secular divergencies obtained in a nonphase-isolated approach[23] as used, for example, in recent implementations of SCF and MCSCF response theory for excited state linear response properties.[13,14]

For the cluster amplitudes Eq. (17) leads to the same equations as obtained from the ground state quasienergy Lagrangian, i.e., the usual zeroth-order cluster equation $e^{(0)}=0$ and the first-order response equations:

$$(\boldsymbol{A}-\omega_A\boldsymbol{1})t^A(\omega_A)=-\xi^A, \tag{28}$$

with the right hand side vectors defined as:

$$\xi^X_\mu=\left(\frac{\partial e_\mu(t,\epsilon)}{\partial\epsilon_X(0)}\right)_0. \tag{29}$$

The zeroth-order equations for the Lagrangian multipliers $\tilde{\bar{N}}^f$, which are obtained from the requirement that $\{\Delta L^f\}_T$ is stationary in the cluster amplitudes, are found as:

$$\tilde{\bar{N}}^f\boldsymbol{A}=-\overline{E^f}(-\omega_f)\boldsymbol{B}E^f(\omega_f). \tag{30}$$

Equations (1)–(30) were formulated for a general coupled cluster model, but are also valid for other nonvariational *ab initio* methods, if the equations for the wave function parameters $e_\mu(t,\epsilon)$ are replaced by the equations for the method under consideration. Expressions for the specific coupled cluster methods CCS, CC2[28] and CCSD are obtained by truncating the cluster amplitudes $t(t,\epsilon)$ and the vectors $\tilde{E}^f(t,\epsilon)$, $\tilde{\bar{E}}^f(t,\epsilon)$ and $\tilde{\bar{N}}^f(t,\epsilon)$ for CCS to the single excitation manifold and for CC2 and CCSD to the single and

double excitation manifold, and by replacing $e_\mu(t,\epsilon) = i(d/dt)t_\mu(t,\epsilon)$ by the respective time-dependent amplitude equations.[28–33]

Before proceeding to the description of the excited state polarizability calculation a few comments on the implementation are warranted. The presented theory is implemented in a local version of the Dalton program[34] using the integral direct CC algorithm as previously described for ground state energies,[35] excitation energies,[36] and ground state linear and nonlinear properties.[30,32,33,37] The solution of the left and right eigenvector equations together with the solution of the first-order amplitude response equations [Eq. (28)] and the $\tilde{\bar{N}}^f(t,\epsilon)$ equations [Eq. (30)] proceeds as discussed in Ref. 33. The new set of equations to be solved in the present study are the excited state response equations [Eq. (26)]. These equations are very similar to the second-order cluster amplitude response equations used in ground state cubic response calculations.[32] The most important modification is that the right hand side vector of the response equations must be projected to the orthogonal complement of the excited reference state f and that the projector $\mathbf{Q}^f$ must also be taken into account whenever the reduced space used in the solution of the linear equations is extended with a new trial vector. The action of the projector $\mathbf{Q}^f$ from the right onto an arbitrary vector $\boldsymbol{\rho}$ reduces in practice to vector operations, which can be evaluated with comparatively low computational costs:

$$\sum_\nu Q^f_{\mu\nu}\rho_\nu = \rho_\mu + E^f_\mu(\omega_f)\left(\sum_\nu \overline{E^f_\nu}(-\omega_f)\rho_\nu\right). \tag{31}$$

The final matrix-vector contractions required for obtaining the difference between the ground and excited state linear response functions [Eq. (19)] are obtained straightforwardly from the contractions required for CC ground state nonlinear response calculations.[30,32]

TABLE I. The ground and excited states structures employed in the calculations on *s*-tetrazine and pyrimidine. Bond lengths are in Ångstrøm and angles are in degrees.

Parameter	S_0	S_1
s-tetrazine		
r_{CH}	1.0726[a]	1.0747[b]
r_{CN}	1.3405[a]	1.3280[b]
r_{NN}	1.3256[a]	1.3166[b]
$\angle_{NCN}$	126.4[a]	121.4[b]
pyrimidine		
$r_{C(2)H}$	1.082[c]	
$r_{C(4)H}$	1.079[c]	
$r_{C(5)H}$	1.087[c]	
$r_{C(5)C(4)}$	1.393[c]	
$r_{C(4)N}$	1.350[c]	
$r_{C(2)N}$	1.328[c]	
$\angle_{CCC}$	117.8[c]	
$\angle_{CCN}$	121.2[c]	
$\angle_{C(5)C(4)H}$	120.9[c]	

[a]Experimental equilibrium structure, Refs. 39, 40.
[b]*Ab initio* CCSD/TZ2P equilibrium structure, Ref. 11.
[c]Experimental equilibrium structure, Ref. 41.

TABLE II. The static dipole polarizability for the ground state and the first excited singlet state of pyrimidine (in a.u.). All results refer to the experimental ground state geometry of pyrimidine given in Table I.

Component	SCF	CCS	CC2	CCSD
		S_0 ground state		
α_{xx}	64.6	69.3	71.1	67.8
α_{yy}	66.5	71.5	74.1	70.2
α_{zz}	36.7	39.7	38.3	37.5
γ[a]		30.7	34.3	31.5
		S_1 excited state		
α_{xx}		111.9	128.6	111.8
α_{yy}		76.0	75.8	71.4
α_{zz}		46.2	44.5	42.2
γ[a]		47.8	57.7	49.4
$\Delta\alpha_{zz}$		6.5	6.2	4.7

[a]$\gamma = (\alpha_{xx}+\alpha_{yy})/2 - \alpha_{zz}$.

III. COMPUTATIONAL DETAILS

In the calculation of the polarizabilities of s-tetrazine and pyrimidine in the S_0 and S_1 states we employed the medium sized POL [5s3p2d/3s2p] basis sets of Sadlej.[38] For *s*-tetrazine we used the experimental ground state geometry from Refs. 39, 40, and for the S_1 ($1\,^1B_{3u}$) excited state the equilibrium structure, optimized by Stanton and Gauss at the CCSD/TZ2P level.[11] For pyrimidine we used the experimental ground state geometry of Ref. 41 for both the ground state and the excited state, since no excited state geometry was available in the literature. The bond distances and angles are given in Table I. For *s*-tetrazine the molecule was placed in the yz plane with the z axis passing through the carbon and hydrogen atoms; the pyrimidine molecule was placed in the xy plane with the y axis coinciding with the molecular C_2 symmetry axis. In the coupled cluster energy and response calculations the molecular orbitals corresponding to the 1*s* orbitals of the carbon and nitrogen atoms were kept frozen.

IV. RESULTS AND DISCUSSION

In Table II we have listed the components of the static dipole polarizability of pyrimidine in the ground state S_0 and the lowest excited state S_1 ($1\,^1B_1$) obtained with the three coupled cluster models CCS, CC2 and CCSD. The dynamic dipole polarizabilities for the two states are shown in Figs.

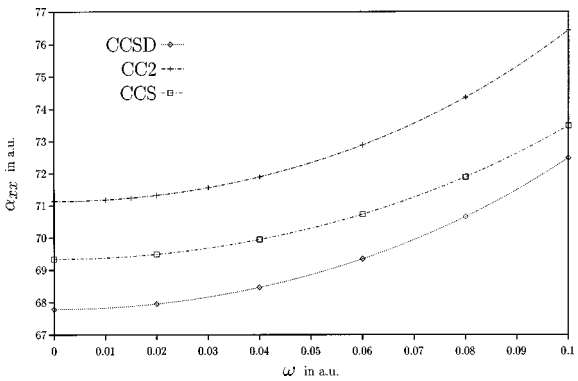


FIG. 1. The dynamic polarizability of pyrimidine in the ground state S_0, α_{xx} component.

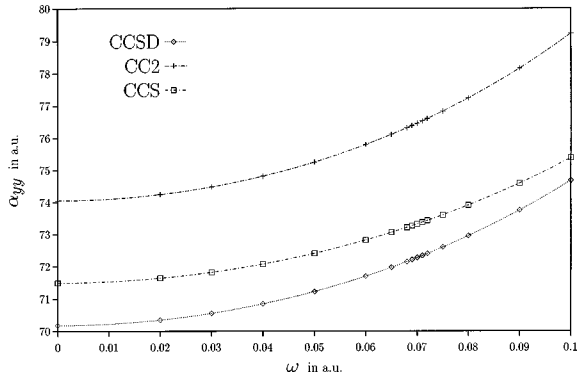


FIG. 2. The dynamic polarizability of pyrimidine in the ground state S_0, α_{yy} component.

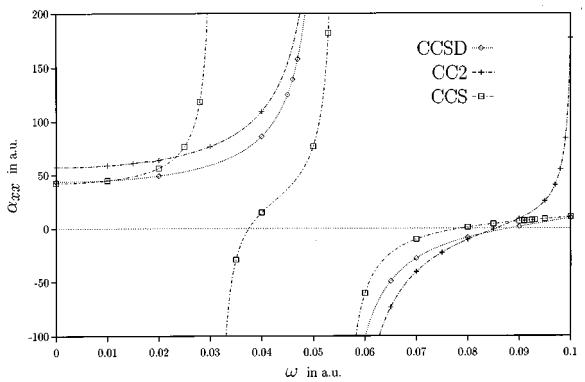


FIG. 4. The change of the dynamic polarizability of pyrimidine upon excitation into the lowest excited singlet state S_1, α_{xx} component.

1–6 for the frequency range $\omega = 0.0-0.1$ a.u. In Table III we give the excitation energies for a few low lying singlet states with symmetries A_1, B_1 and A_2, i.e., states that can be reached from S_1 by dipole-allowed transitions and which therefore are important for the polarizability of this state. For the excitation energies we find in agreement with the results of earlier studies[42,43] that the CC2 model gives excitation energies which are considerably improved compared to the CCS level. This is manifested by the differences to the CCSD results which for CC2 in most cases are much smaller than for CCS. For the states below 7 eV the CC2 excitation energies differ by not more than 0.3 eV from the CCSD results, while the CCS model gives for some of these states excitation energies which are wrong by more than 1 eV. This is also the case for the S_1 state for which we are investigating the polarizability. The calculated vertical CCSD excitation energies are slightly higher than the position of the band maxima found experimentally. The agreement between theory and experiment, however, is as good as can be expected considering the uncertainty in the calculated excitation energies introduced by the relatively small one-electron basis set and by the differences between rigorous vertical excitation energies and the observed position for the band maxima.

Surprisingly, we find that the CCS polarizabilities for the ground state and for the excited S_1 state are close to the values obtained with CCSD. For the static polarizabilities we obtain with the CC2 model no improvement upon the CCS results. For the α_{xx} component of the excited S_1 state polarizability the difference compared to CCSD even increases at the CC2 level to more than 15%.

The situation changes dramatically if we consider the frequency-dependence. Due to the large errors in the CCS excitation energies the dynamic polarizabilities obtained in CCS get large errors in the dispersion compared with the CCSD results. In particular for the excited S_1 state the errors in the poles at the CCS level are so large that the CCS polarizabilities over a wide frequency range hardly have anything in common with the results obtained with the correlated CC2 and CCSD models. At the CC2 level the pole structure of the dynamic polarizabilities is very similar to that obtained in CCSD. Nevertheless, the quantitative differences between the CC2 and the CCSD results for the dynamic polarizabilities are rather large.

The theoretically most intensively studied excited state polarizability is probably the polarizability of *s*-tetrazine in the S_1 state.[10,11,44–46] Heitz, Weidauer, and Hese[6] used in 1991 laser Stark spectroscopy to measure the polarizability anisotropy $\gamma = (\alpha_{zz} + \alpha_{yy})/2 - \alpha_{xx}$ of the ground state and the S_1 state and the shifts of the isotropic polarizability $\bar{\alpha}$ and the out-of-plane component α_{xx} for the transition $S_1 \leftarrow S_0$. While the experimental value for the shift in the isotropic polarizability is in qualitative good agreement with the results obtained in several *ab initio* studies,[10,11,46] the anisot-

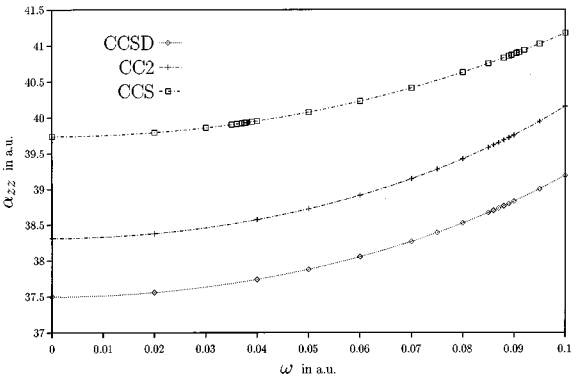


FIG. 3. The dynamic polarizability of pyrimidine in the ground state S_0, α_{zz} component.

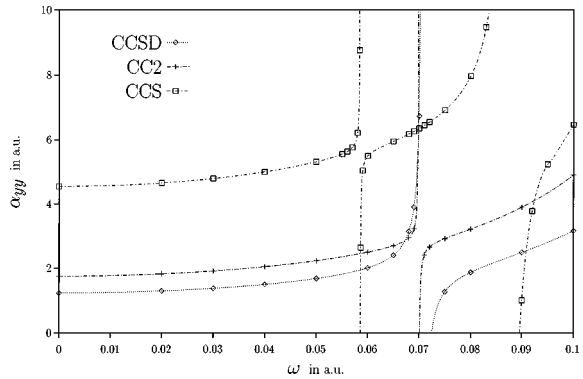


FIG. 5. The change of the dynamic polarizability of pyrimidine upon excitation into the lowest excited singlet state S_1, α_{yy} component.

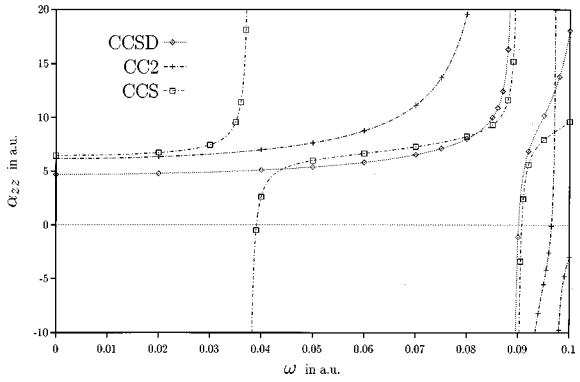


FIG. 6. The change of the dynamic polarizability of pyrimidine upon excitation into the lowest excited singlet state S_1, α_{zz} component.

ropy of the ground state polarizability and the shift of the out-of-plane component upon excitation are in strong disagreement with the results of the *ab initio* calculations (see Table IV).

We have employed the CCSD response approach to calculate the static polarizability of *s*-tetrazine in the ground state and in the excited S_1 state. The results are summarized in Table IV together with the experimental values and results of previous *ab initio* calculations. For all three components of the ground state polarizability we obtained results similar to the finite field CCSD calculations of Stanton and Gauss[11] and the finite field CASPT2 calculations of Schütz *et al.*[10] The finite field calculations of Stanton and Gauss correspond to an orbital-relaxed CCSD approach where also the Hatree–Fock orbitals can respond to the perturbations, while in the coupled cluster response approach only the cluster amplitudes respond to the external fields.

For the out-of-plane component α_{xx} in the S_1 excited state the CCSD response result is close to the CASPT2 value[10] and the CCSD finite field result.[11] For the in-plane components α_{zz} and α_{yy} the differences between the individual *ab initio* methods are somewhat larger, showing that these components are more sensitive to the correlation treatment. The geometry effects originating from shifts in the bond lengths and angles upon excitation are for all three polarizability components small, only of the order of a few percent.

As in previous *ab initio* investigations, we find agreement with the experimental results for the shift of the isotropic polarizability $\Delta\overline{\alpha}$ and for the polarizability anisotropy in the S_1 state, but large discrepancies for the anisotropy of the ground state polarizability and for the shift of the out-of-plane component α_{xx}. This supports the conclusions drawn in Ref. 10, where a misassignment of the symmetry axes in the experimental work was suspected.

TABLE III. Calculated vertical excitation energies to the lowest singlet states in pyrimidine (in eV), compared to positions of band maxima in VUV measurements.

State	CCS	CC2	CCSD	Exp.
		S_0 ground state		
$2\,^1A_1$	6.86	6.75	7.01	6.7[b]
$3\,^1A_1$	8.28	7.02	7.45	
$4\,^1A_1$	8.72	7.48	7.73	7.6[b]
$1\,^1B_1$	5.83	4.37	4.59	4.2[a]
$2\,^1B_1$	7.42	6.28	6.51	6.0[b]
$3\,^1B_1$	8.21	7.34	7.42	
$1\,^1A_2$	6.68	4.88	5.16	4.6[a]
$2\,^1A_2$	7.33	5.84	6.03	5.7[c]
$3\,^1A_2$	8.33	7.12	7.74	

[a]Reference 48.
[b]Reference 49.
[c]Reference 50.

V. CONCLUSIONS

We have reported an implementation of coupled cluster response theory for static and dynamic polarizabilities of excited singlet states for the coupled cluster models CCS, CC2 and CCSD. The approach is based on a quasienergy La-

TABLE IV. The static dipole polarizability for the ground and first excited singlet state of *s*-tetrazine (in a.u.).

Component	SCF[a]	CASSCF[b]	CASPT2[c]	CCSD[d]	CCSD resp.[e]	Experiment[f]
			S_0 ground state			
α_{xx}	29.8	29.8	32.6	32.0	32.7	
α_{yy}	52.7	53.4	55.1	54.4	56.0	
α_{zz}	57.4	53.8	60.0	59.0	60.7	
γ[g]	25.2	23.8	25.0	24.7	26.7	5.4
			S_1 excited state			
α_{xx}	28.7	38.2	32.4	31.3	31.9 (31.1)	
α_{yy}	70.8	74.4	67.2	74.0	80.1 (83.2)	
α_{zz}	63.7	66.6	66.0	63.9	61.5 (65.7)	
γ[g]	38.4	42.3	34.2	37.6	41.1 (43.4)	45.2
$\Delta\alpha_\perp$	−1.1	−1.6	−0.2	−0.7	−0.9 (−0.7)	−17.5

[a]SCF response calculation in a $[4s4p2d/2s1p]$ basis, Ref. 46.
[b]CASSCF response calculation in a $[4s4p2d/2s1p]$ basis, Ref. 46.
[c]CASPT2 finite field calculation in Sadlej's $[5s3p2d/3s2p]$ POL basis, Ref. 10.
[d]CCSD finite field calculations in Sadlej's $[5s3p2d/3s2p]$ POL basis, Ref. 11.
[e]This work, CCSD response calculation, the number in parentheses were obtained without geometry relaxation for the S_1 state.
[f]Laser Stark spectroscopy, Ref. 7.
[g]Polarizability anisotropy parameter γ is defined as $\gamma=0.5(\alpha_{yy}+\alpha_{zz})-\alpha_{xx}$.

grangian for the excited states and a phase-isolated parametrization of the excited state wave function. Secular divergent terms are thereby removed from the response function and the response equations become numerically stable in the static limit. An application to the frequency-dependent polarizability of the S_1 state of pyrimidine demonstrates that the results for the excited state polarizabilities are very sensitive to the accuracy of the excitation energies. Reliable results require correlated wave function models and can only be expected for the lowest excited states and only if these states are well separated from the other excited states. This is also corroborated by the results of a study of the polarizability of benzene in the lowest excited states.[47]

The results obtained with the CCSD response approach for the static polarizability of *s*-tetrazine in the ground state and the excited S_1 state support the findings of earlier *ab initio* studies which suspected a misassignment of the symmetry axes in the experimental work.

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[1] R. G. E. Morales, J. Chem. Phys. **86**, 2550 (1982).
[2] N. Ghoneim and P. Suppan, J. Chem. Soc., Faraday Trans. **86**, 2079 (1990).
[3] H. K. Sinha, P. C. P. Thomson, and K. Yates, Can. J. Chem. **68**, 1507 (1990).
[4] P. T. Chongwain, Spectrochim. Acta A **47**, 713 (1991).
[5] K. Tanaka, H. Ito, K. Harada, and T. Tanaka, J. Chem. Phys. **80**, 5893 (1984).
[6] S. Heitz, D. Weidauer, and A. Hese, Chem. Phys. Lett. **176**, 55 (1991).
[7] S. Heitz, D. Weidauer, and A. Hese, J. Chem. Phys. **95**, 7952 (1991).
[8] S. Heitz, D. Weidauer, and B. Rosenow, J. Chem. Phys. **96**, 976 (1992).
[9] I. Iweibo, Spectrochim. Acta A **47**, 705 (1991).
[10] M. Schütz, J. Hutter, and H. P. Lüthi, J. Chem. Phys. **103**, 7048 (1995).
[11] J. F. Stanton and J. Gauss, J. Chem. Phys. **104**, 9859 (1996).
[12] J. Pipin and D. M. Bishop, Phys. Rev. A **47**, R4571 (1993).
[13] P. Norman, D. Jonsson, O. Vahtras, and H. Ågren, Chem. Phys. **203**, 23 (1996).
[14] D. Jonsson, P. Norman, and H. Ågren, J. Chem. Phys. **105**, 6401 (1996).
[15] H. Koch and P. Jørgensen, J. Chem. Phys. **93**, 3333 (1990).
[16] J. F. Stanton and J. Gauss, J. Chem. Phys. **99**, 8840 (1993).
[17] J. F. Stanton and J. Gauss, J. Chem. Phys. **100**, 4695 (1994).
[18] J. F. Stanton and J. Gauss, Theor. Chim. Acta **91**, 267 (1995).
[19] J. F. Stanton and J. Gauss, J. Chem. Phys. **103**, 7401 (1995).
[20] H. J. Monkhorst, Int. J. Quantum Chem. **S11**, 421 (1977).
[21] O. Christiansen, P. Jørgensen, and C. Hättig, Int. J. Quantum Chem. **68**, 1 (1998).
[22] C. Hättig, O. Christiansen, and P. Jørgensen, J. Chem. Phys. **108**, 8331 (1998).
[23] C. Hättig and P. Jørgensen, J. Chem. Phys. **109**, 9219 (1998), preceding paper.
[24] P. G. Szalay, Int. J. Quantum Chem. **55**, 151 (1995).
[25] T. Helgaker and P. Jørgensen, ''Calculation of geometrical derivatives in molecular electronic structure theory,'' in *Methods in Computational Physics*, edited by S. Wilson and G. H. F. Diercksen (Plenum, New York, 1992), pp. 353–421.
[26] T. Helgaker and P. Jørgensen, Theor. Chim. Acta **75**, 111 (1989).
[27] P. Jørgensen and T. Helgaker, J. Chem. Phys. **89**, 1560 (1988).
[28] O. Christiansen, H. Koch, and P. Jørgensen, Chem. Phys. Lett. **243**, 409 (1995).
[29] O. Christiansen, H. Koch, and P. Jørgensen, J. Chem. Phys. **103**, 7429 (1995).
[30] C. Hättig, O. Christiansen, H. Koch, and P. Jørgensen, Chem. Phys. Lett. **269**, 428 (1997).
[31] C. Hättig, O. Christiansen, and P. Jørgensen, J. Chem. Phys. **107**, 10592 (1997).
[32] C. Hättig, O. Christiansen, and P. Jørgensen, Chem. Phys. Lett. **282**, 139 (1998).
[33] O. Christiansen, A. Halkier, H. Koch, P. Jørgensen, and T. Helgaker, J. Chem. Phys. **108**, 2801 (1998).
[34] T. Helgaker, H. J. A. Jensen, P. Jørgensen, J. Olsen, K. Ruud, H. Ågren, T. Andersen, K. L. Bak, V. Bakken, O. Christiansen, P. Dahle, E. K. Dalskov, T. Enevoldsen, B. Fernandez, H. Heiberg, H. Hettema, D. Jonsson, S. Kirpekar, R. Kobayashi, H. Koch, K. V. Mikkelsen, P. Norman, M. J. Packer, T. Saue, P. R. Taylor, and O. Vahtras, Dalton—An electronic structure program, release 1.0, 1997.
[35] H. Koch, O. Christiansen, P. Jørgensen, A. S. de Merás, and T. Helgaker, J. Chem. Phys. **106**, 1808 (1997).
[36] O. Christiansen, H. Koch, A. Halkier, P. Jørgensen, T. Helgaker, and A. M. Sanchez de Meras, J. Chem. Phys. **105**, 6921 (1996).
[37] A. Halkier, H. Koch, O. Christiansen, P. Jørgensen, and T. Helgaker, J. Chem. Phys. **107**, 849 (1997).
[38] A. J. Sadlej, Collect. Czech. Chem. Commun. **53**, 1995 (1988).
[39] V. A. Job and K. K. Innes, J. Mol. Spectrosc. **71**, 299 (1978).
[40] K. K. Innes, D. V. Brumbaugh, and L. A. Franks, Chem. Phys. **59**, 439 (1981).
[41] S. Cradock, P. B. Liescheski, D. W. H. Rankin, and H. E. Robertson, J. Am. Chem. Soc. **110**, 2758 (1988).
[42] H. Koch, O. Christiansen, P. Jørgensen, and J. Olsen, Chem. Phys. Lett. **244**, 75 (1995).
[43] O. Christiansen, H. Koch, P. Jørgensen, and J. Olsen, Chem. Phys. Lett. **256**, 185 (1996).
[44] T. K. Ha, Mol. Phys. **29**, 1829 (1975).
[45] F. Mulder, G. van Dijk, and C. Huiszoon, Mol. Phys. **38**, 577 (1979).
[46] D. Jonsson, P. Norman, and H. Ågren, Chem. Phys. **244**, 201 (1997).
[47] Ove Christiansen, C. Hättig, and P. Jørgensen, Spectrochim. Acta (in press).
[48] A. Bolovinos, P. Tsekeris, J. Philis, E. Pantos, and B. Andritsopoulos, J. Mol. Spectrosc. **103**, 240 (1984).
[49] M. H. Palmer, I. C. Walker, M. F. Guest, and A. Hopkirk, Chem. Phys. **147**, 19 (1990).
[50] P. R. Callis, T. W. Scott, and A. C. Albrecht, J. Chem. Phys. **75**, 5640 (1981).