17 February 1995

ELSEVIER

Chemical Physics Letters 233 (1995) 359–370

CHEMICAL PHYSICS LETTERS

Correlated frequency-dependent polarizabilities and dispersion coefficients in the time-dependent second-order Møller–Plesset approximation

Christof Hättig, Bernd Artur Heß

Institut für Physikalische und Theoretische Chemie der Universität Bonn, Wegelerstraße 12, D-53115 Bonn 1, Germany

Received 17 November 1994

Abstract

A new method for the calculation of correlated frequency-dependent polarizabilities by the use of time-dependent second-order Møller–Plesset perturbation theory is presented. Within this method the dynamic polarizabilities are defined as second derivatives of the MP2 energy with respect to the strengths of two oscillating external fields. This definition assures the symmetry of mixed polarizabilities and leads to the same second-order pole structure as the diagrammatic double-perturbation MBPT methods. As a derivative method this approach becomes equivalent to finite field MP2 calculations in the static limit. We report applications to helium and neon.

1. Introduction

Although in recent years much effort has been devoted to the development of methods for the calculation of accurate dynamic response properties [1–11], this is still a problem far from standard for methods which account for the electron correlation, as illustrated by the manifold of Ansatzes used in the literature. A problem which arises for methods which are not fully variational, i.e. which do not fulfil the Hellmann–Feyman theorem, is the arbitrariness in the definition of the dynamic response properties.

Especially for approaches based on many-body perturbation theory (MBPT) different definitions of the dynamic polarizabilities are proposed in the literature. Wormer and co-workers use a double-perturbation expansion of the multipole expectation value $\langle \Psi(\omega, t) | \hat{Q}_{lm} | \Psi(\omega, t) \rangle$ for their SDT-MBPT method [4,9]; the same is done by Veseth in his diagrammatic MBPT method [12]. Rice and Handy [8] define their dynamic polarizabilities as second derivatives of a MP2 pseudo-energy with respect to one frequency-dependent and one static electric field, while Aiga et al. [13,14] proposed to define the dynamic polarizabilities as second derivatives of the quasi-energy with respect to two oscillating electric fields with the same frequency.

The expressions for the MP2 dynamic polarizabilities derived by the use of these three definitions not only differ in the correlation contribution to the oscillator strengths, but also in their pole structure, because in the derivative expressions given by Rice and Handy and by Aiga et al. the second-order poles (i.e. those corresponding to double excitations) are missing, but are present in the diagrammatic expansion used by Wormer and co-workers and also by Veseth.

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SSDI 0009-2614(94)01487-6

We therefore developed and implemented a new method for the calculation of dynamic polarizabilities by second-order time-dependent Møller–Plesset perturbation theory, where we define the frequency-dependent linear response properties as second derivatives of the MP2 energy, i.e. the expansion of the energy expectation value, with respect to the strengths of two external frequency-dependent fields. By this definition our derivative MP2 method becomes equivalent to the double perturbational MBPT method, if one truncates the diagrammatic expansion of the derivative expressions in second-order in the electron fluctuation potential. In particular we get the second-order poles which are missing in the pseudo-energy method of Rice and Handy.

In Section 2 we discuss briefly the definition of dynamic second-order properties for Møller–Plesset perturbation theory. In Section 3 we derive the time-dependent MP2 correlation corrections to the TDHF approximation and a time-dependent MP2 energy Lagrangian. In sections 4–6 the necessary response equations and an explicit expression for the MP2 dynamic polarizability are determined. Using the Lagrangian technique developed by Jørgensen and Helgaker [15,16] and Helgaker et al. [17] together with a non-canonical representation for the derivatives of the molecular orbitals, computationally efficient and numerical stable expressions are obtained.

2. Definition of the MP2 dynamic polarizabilities

There are, in general, two ways to define second-order properties. One is based on the expansion of the expectation values in the presence of one external field,

$$\hat{H} = \hat{H}^{(0)} + \hat{h}_W^{(1)}(\omega, t), \qquad \hat{h}_W^{(1)}(\omega, t) = \left[f_W(\omega)\, \mathrm{e}^{+\mathrm{i}\omega t} + f_W(-\omega)\, \mathrm{e}^{-\mathrm{i}\omega t} \right] \hat{W},$$
$$\langle \hat{Q} \rangle(\omega, t) = Q_0 + \alpha_{QW}(\omega; -\omega) \left[f(\omega)\, \mathrm{e}^{\mathrm{i}\omega t} + f(-\omega)\, \mathrm{e}^{-\mathrm{i}\omega t} \right] + \ldots, \tag{1}$$

and leads to the definition of the polarizability $\alpha_{QW}(\omega; -\omega)$ as the linear response of the expectation value $\langle \hat{Q} \rangle$ of an arbitrary operator $\hat{Q}$, corresponding to a molecular property, to the oscillating field described by the operator $\hat{W}$.

The other possibility is to define the second-order properties by an expansion of the energy in the presence of two external fields,

$$\begin{aligned}
&\hat{H} = \hat{H}^{(0)} + \hat{h}_Q^{(1)}(\omega_Q t) + \hat{h}_W^{(1)}(\omega_W t), \\
&E(\omega_Q, \omega_W, t) \\
&\quad = E_0 + \langle \hat{Q} \rangle \left[f_Q(\omega_Q) \exp(+\mathrm{i}\omega_Q t) + f_Q(-\omega_Q) \exp(-\mathrm{i}\omega_Q t) \right] \\
&\qquad + \langle \hat{W} \rangle \left[f_W(\omega_W) \exp(+\mathrm{i}\omega_W t) + f_W(-\omega_W) \exp(-\mathrm{i}\omega_W t) \right] \\
&\qquad - \tfrac{1}{2} \alpha_{QQ}(-\omega_Q; \omega_Q) \left[f_Q(\omega_Q) \exp(+\mathrm{i}\omega_Q t) + f_Q(-\omega_Q) \exp(-\mathrm{i}\omega_Q t) \right]^2 \\
&\qquad - \tfrac{1}{2} \left[\alpha_{QW}(-\omega_Q; \omega_Q) + \alpha_{QW}(-\omega_W; \omega_W) \right] \left[f_Q(\omega_Q) \exp(+\mathrm{i}\omega_Q t) + f_Q(-\omega_Q) \exp(-\mathrm{i}\omega_Q t) \right] \\
&\qquad \times \left[f_W(\omega_W) \exp(+\mathrm{i}\omega_W t) + f_W(-\omega_W) \exp(-\mathrm{i}\omega_W t) \right] \\
&\qquad - \tfrac{1}{2} \alpha_{WW}(-\omega_W; \omega_W) \left[f_W(\omega_W) \exp(+\mathrm{i}\omega_W t) + f_W(-\omega_W) \exp(-\mathrm{i}\omega_W t) \right]^2 + \ldots .
\end{aligned} \tag{2}$$

Hence it follows that the frequency-dependent polarizability $\alpha_{QW}(\omega, -\omega)$ can alternatively be defined by the equation

$$\alpha_{QW}(\omega, -\omega) = -\left. \frac{\partial^2 E}{\partial f_Q(\omega) \partial f_W(-\omega)} \right|_0 . \tag{3}$$

For methods which obey the Hellmann–Feynman theorem, both definitions are equivalent, but for Møller–Plesset perturbation theory the two definitions lead to different expressions for the second-order properties. For static polarizabilities it has been shown by Sadlej [18] in a diagrammatic order-by-order analysis that the double-perturbation treatment of the external field and the correlation effects with reference to the unperturbed SCF state based on the expansion (1) and the perturbational calculation of the correlation corrections to the results of the coupled Hartree–Fock (CHF) theory, which is equivalent to the definition of the polarizability as a second derivative of the energy, differ only in the treatment of the so called *apparent correlation* contributions. In the frequency-dependent case this relation is retained if one uses the derivative expression (3) which yields the same second-order pole structure as the double-perturbation approach.

3. Time-dependent Møller–Plesset perturbation theory

If $\Psi_0^{(0)}$ is a time-independent eigenfunction of the unperturbed Hamiltonian $\hat{H}^{(0)}$ and $\{\Psi_n^{(0)}\}$ a basis for the orthogonal complement of $\Psi_0^{(0)}$, the time-dependent eigenfunction of $\hat{H}$ with a nonvanishing coefficient of $\Psi_0^{(0)}$ can be parametrized as [19]

$$|\bar{\Psi}_0(t)\rangle = \exp\left(-\mathrm{i}\int_{t_0}^{t} \mathrm{d}t'\ W(t')\right)|\tilde{\Psi}_0(t)\rangle, \tag{4}$$

with

$$|\tilde{\Psi}_0(t)\rangle = \left(|\Psi_0^{(0)}\rangle + \sum_{n\neq 0} d_n(t)\,|\Psi_n^{(0)}\rangle\right)/N(t). \tag{5}$$

The function $W(t)$ in the phase factor is often referred to as the quasi-energy, because for a time-independent $\hat{H}$ and a normalized wavefunction it becomes equal to the energy expectation value. By isolating this phase factor, the time-dependent equations are brought into a form which in the static limit becomes identical to the usual time-independent equations. So the Schrödinger equation for $|\tilde{\Psi}_0(t)\rangle$ is

$$\hat{H}\,|\tilde{\Psi}_0(t)\rangle = [\mathrm{i}(\partial/\partial t) - W(t)]\,|\tilde{\Psi}_0(t)\rangle. \tag{6}$$

Multiplying (6) with an arbitrary variation $|\delta\tilde{\Psi}_0(t)\rangle = \alpha\,|\tilde{\Psi}_0(t)\rangle + |\delta\tilde{\Psi}_0(t)^{\perp}\rangle$, where $|\delta\tilde{\Psi}_0(t)^{\perp}\rangle$ is orthogonal to $|\tilde{\Psi}_0(t)\rangle$, one obtains the equation for the quasi-energy

$$W(t) = \langle\tilde{\Psi}_0(t)\,|\,\hat{H} - \mathrm{i}(\partial/\partial t)\,|\tilde{\Psi}_0(t)\rangle, \tag{7}$$

and the Frenkel principle in the formulation of Moccia [20]

$$\langle\delta\tilde{\Psi}_0(t)^{\perp}\,|\,\hat{H} - \mathrm{i}(\partial/\partial t)\,|\tilde{\Psi}_0(t)\rangle = 0 \tag{8}$$

as the time-dependent variation condition.

3.1. The TDHF method

In the closed-shell TDHF method the time-dependent wavefunction is approximated by a single determinant, which can be parametrized in its phase-isolated form as

$$|\tilde{0}(\omega, t)\rangle = \exp[-\hat{\kappa}(\omega, t)]\,|0\rangle, \tag{9}$$

where $|0\rangle$ denotes the unperturbed SCF wavefunction and

$$\hat{\kappa}(\omega, t) = \sum_{ai}\left[\kappa_{ai}(\omega, t)\hat{E}_{ai} - \kappa_{ai}^{*}(\omega, t)\hat{E}_{ia}\right] \tag{10}$$

is the orbital rotation operator where $\hat{E}_{ai}$ are the usual generators of the unitary group. Here and in the following, we use the indices *ijkl* to denote occupied orbitals, *abcd* to denote virtual orbitals, and *pqrs* for general orbitals. Because the TDHF equations for the redundant occupied–occupied and virtual–virtual rotation become singular or numerical unstable, when the unperturbed Hartree–Fock solution contains degenerate or nearly degenerate orbitals, we use only the non-redundant occupied–virtual rotations, i.e. we do not insist on the canonical representation for the perturbed TDHF wavefunction.

In the time-dependent basis

$$\tilde{E}_{pq}(\omega, t) = \exp[-\hat{\kappa}(\omega, t)]\hat{E}_{pq}\exp[\hat{\kappa}(\omega, t)], \tag{11}$$

a general variation $|\tilde{0}^{\perp}\rangle$ can be written as

$$|\delta\tilde{0}^{\perp}\rangle = \sum_{ai}\left(\eta_{ai}\tilde{E}_{ai} - \eta_{ai}^{*}\tilde{E}_{ia}\right)|\tilde{0}\rangle. \tag{12}$$

Introducing Eqs. (9) and (12) into the Frenkel principle (8), one obtains the time-dependent variation condition for the TDHF wavefunction,

$$\langle\tilde{0}|\left[\tilde{E}_{\mu}, \left(\hat{H} - \mathrm{i}\frac{\partial}{\partial t}\right)\right]|\tilde{0}\rangle = 0, \qquad \mu \in \{(ai), (ia)\}. \tag{13}$$

3.2. The time-dependent MPPT equations

In the Møller–Plesset perturbation theory $\hat{H}$ is partitioned into the Fock operator $\hat{F}$ as zeroth-order Hamiltonian and the fluctuation potential $\hat{V}$,

$$\hat{H} = \hat{F} + \hat{V}. \tag{14}$$

Both the quasi-energy and the wavefunction are expanded in orders of the fluctuation potential,

$$W(t) = \sum_{n=0} W_n(t), \tag{15}$$

$$|\tilde{\Psi}_0(t)\rangle = |\tilde{0}\rangle + \sum_{n=1}\lambda^n|\tilde{\Psi}_0^{(n)}(t)\rangle, \tag{16}$$

where $|\tilde{0}\rangle$ is the solution of the TDHF Eq. (13) and the zeroth-order quasi-energy is given by $W_0 = \langle\tilde{0}|\hat{F} - \mathrm{i}(\partial/\partial t)|\tilde{0}\rangle$. We use the usual intermediate normalization $\langle\tilde{0}|\tilde{\Psi}_0\rangle = 1$, so that the first-order Møller–Plesset correction to the wavefunction can be expanded in the set of all double excitations $\{|\tilde{u}\rangle\}$ from the TDHF reference state $|\tilde{0}\rangle$,

$$|\tilde{\Psi}_0^{(1)}(t)\rangle = \sum_{u\neq 0} a_u(t)\,|\tilde{u}(t)\rangle. \tag{17}$$

Inserting this expansion into the time-dependent Schrödinger equation in its phase-isolated form (6) and projecting onto $\{\langle\tilde{v}|\}$ we find as equation for the amplitudes

$$\sum_{u\neq 0}\langle\tilde{v}|\left(\hat{F} - W_0 - \mathrm{i}\frac{\partial}{\partial t}\right)a_u|\tilde{u}\rangle + \langle\tilde{v}|\hat{V}|\tilde{0}\rangle = 0. \tag{18}$$

In contrast to the corresponding equation of Aiga et al. Eq. (18) contains a term involving the derivatives of the amplitudes with respect to the time. It is this derivative which introduces the second-order poles into the frequency-dependent MP1 wavefunction and the frequency-dependent MP2 polarizabilities.

We define the time-dependent MP2 energy contributions by the expansion of the expectation value of $\hat{H}$ in orders of the fluctuation potential,

$$E(t) = \langle \tilde{\Psi}_0(t) \,|\, \hat{H}(t) \,|\, \tilde{\Psi}_0(t) \rangle / \langle \tilde{\Psi}_0(t) \,|\, \tilde{\Psi}_0(t) \rangle, \tag{19}$$

$$E_{\mathrm{TDHF}} = E_0 + \Delta E_{\mathrm{MP1}} = \langle \tilde{0} \,|\, \hat{H} \,|\, \tilde{0} \rangle, \tag{20}$$

$$\Delta E_{\mathrm{MP2}} = \tfrac{1}{2}\Big(\langle \tilde{\Psi}_0^{(1)}(t) \,|\, \hat{V} \,|\, \tilde{0} \rangle + \langle \tilde{0} \,|\, \hat{V} \,|\, \tilde{\Psi}_0^{(1)}(t) \rangle \Big). \tag{21}$$

3.3. The time-dependent MP2 energy Lagrangian

In the Lagrangian technique developed by Jørgensen and Helgaker [15,17] the original expression for the energy is replaced by a variational Lagrange function, constructed from the energy functional and the constraints for its parameters. The MP2 energy functional is given by Eq. (21) and as constraints we have to consider the TDHF Eq. (13) and the equations for the amplitudes (18). In the time-dependent case the calculation of derivatives can be further simplified by the introduction of the equations for the conjugated amplitudes,

$$\langle \tilde{\Psi}_0^{(1)}(t) \,| = \sum_{v \neq 0} a_v^\dagger(t) \langle \tilde{v}(t) \,|, \tag{22}$$

$$\sum_{v \neq 0} \left(a_v^\dagger \langle \tilde{v} \,|\, \hat{F} - W_0 \,|\, \tilde{u} \rangle - \mathrm{i} \left\langle \frac{\partial}{\partial t} \left(a_v^\dagger \right)^* \tilde{v} \middle| \tilde{u} \right\rangle \right) + \langle \tilde{0} \,|\, \hat{V} \,|\, \tilde{u} \rangle = 0, \tag{23}$$

as additional constraints, so that the amplitudes $\boldsymbol{a}$ and their conjugated counterparts $\boldsymbol{a}^\dagger$ can be treated as independent variables. Thus we use as time-dependent Møller–Plesset energy Lagrangian

$$\begin{aligned} L_{\mathrm{MP2}}\left(\kappa, \zeta, \boldsymbol{a}, \boldsymbol{a}^\dagger, \bar{\boldsymbol{a}}, \bar{\boldsymbol{a}}^\dagger\right) = {} & \tfrac{1}{2} \sum_{u \neq 0} \langle \tilde{0} \,|\, \hat{V} \,|\, \tilde{u} \rangle a_u + \tfrac{1}{2} \sum_{v \neq 0} a_v^\dagger \langle \tilde{v} \,|\, \hat{V} \,|\, \tilde{0} \rangle \\ & + \tfrac{1}{2} \sum_{v \neq 0} \bar{a}_v \left[\sum_{u \neq 0} \left(a_u \langle \tilde{v} \,|\, \hat{F} - W_0 \,|\, \tilde{u} \rangle - \langle \tilde{v} \,|\, \mathrm{i} \frac{\partial}{\partial t} a_u \,|\, \tilde{u} \rangle \right) + \langle \tilde{v} \,|\, \hat{V} \,|\, \tilde{0} \rangle \right] \\ & + \tfrac{1}{2} \sum_{u \neq 0} \bar{a}_u^\dagger \left[\sum_{v \neq 0} \left(a_v^\dagger \langle \tilde{v} \,|\, \hat{F} - W_0 \,|\, \tilde{u} \rangle - \left\langle \mathrm{i} \frac{\partial}{\partial t} \left(a_v^\dagger \right)^* \tilde{v} \middle| \tilde{u} \right\rangle \right) + \langle \tilde{0} \,|\, \hat{V} \,|\, \tilde{u} \rangle \right] \\ & + \sum_\mu \zeta_\mu \langle \tilde{0} \,| \left[\tilde{E}_\mu, \hat{H} - \mathrm{i} \frac{\partial}{\partial t} \right] | \tilde{0} \rangle, \end{aligned} \tag{24}$$

where the Lagrange multipliers ζ_μ, $\bar{a}_v$ and $\bar{a}_u^\dagger$ are determined by the requirement that L_{MP2} is stationary in all its variables.

By expanding the parameters κ, μ, a_v and $a_u^\dagger$ as well as the multipliers ζ_μ, $\bar{a}_v$ and $\bar{a}_u^\dagger$ in a Taylor series we will derive in the next three sections the necessary equations for the first and the second derivatives of L_{MP2} with respect to the strengths of the external electric fields.

4. Calculation of the field-independent quantities

4.1. The unperturbed amplitudes and the MP2 energy

It is convenient to calculate the amplitudes and the MP2 energy of the unperturbed system in the canonical representation, since the unperturbed Fock matrix

$$F_{pq}^{(0)} = \langle 0 \,| \sum_\sigma \left[\hat{a}_{p\sigma}^\dagger, \left[\hat{a}_{q\sigma}, \hat{H}^{(0)} \right] \right]_+ | 0 \rangle = \delta_{pq} \epsilon_p, \tag{25}$$

and the matrix representation of $\hat{G} = \hat{F}^{(0)} - \langle 0 | \hat{F}^{(0)} | 0 \rangle$ then become diagonal,

$$\langle {}^{ab}_{ij} | \hat{G} | {}^{ab}_{ij} \rangle = \epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j \equiv -\Delta_{iajb}. \tag{26}$$

By introducing the matrix notation

$$V^{(0)}_{vu} = \langle v | \hat{V} | u \rangle \qquad \text{and} \qquad G^{(0)}_{vu} = \langle v | \hat{G} | u \rangle, \tag{27}$$

we obtain for the unperturbed amplitudes and their conjugated counterparts

$$a^{(0)}_u = -V^{(0)}_{u0}/G^{(0)}_{uu} \qquad \text{and} \qquad a^{(0)\dagger}_u = -V^{(0)}_{0u}/G^{(0)}_{uu} \tag{28}$$

respectively, and the MP2 energy reads

$$\Delta E_{\mathrm{MP2}} = \sum_{u \neq 0} -\frac{V^{(0)}_{0u} V^{(0)}_{u0}}{G^{(0)}_{uu}} = \sum_{iajb} \frac{g_{iajb} k_{iajb}}{\Delta_{iajb}}, \tag{29}$$

where g_{pqrs} are usual two-electron integrals in Mulliken notation and $k_{pqrs} = 2 g_{pqrs} - g_{psrq}$.

4.2. The equations for the Lagrange multipliers

The equations for the Lagrange multipliers $\boldsymbol{\zeta}$, $\bar{\boldsymbol{a}}$ and $\bar{\boldsymbol{a}}^\dagger$ are obtained by requiring the MP2 energy Lagrangian (24) to be stationary in the parameters $\boldsymbol{\kappa}$, $\boldsymbol{a}$ and $\boldsymbol{a}^\dagger$, respectively

$$\partial L_{\mathrm{MP2}}/\partial a_u = 0, \qquad \partial L_{\mathrm{MP2}}/\partial a^\dagger_v = 0, \qquad \partial L_{\mathrm{MP2}}/\partial \kappa_\nu = 0. \tag{30}$$

For the zeroth-order multipliers $\bar{a}^{(0)}$ and $\bar{a}^{(0)\dagger}$ one obtains the equations

$$\sum_{v \neq 0} \bar{a}^{(0)}_v \langle v | \hat{G} | u \rangle + \langle 0 | \hat{V} | u \rangle = 0, \tag{31}$$

$$\sum_{u \neq 0} \bar{a}^{(0)\dagger}_u \langle v | \hat{G} | u \rangle + \langle v | \hat{V} | 0 \rangle = 0, \tag{32}$$

so that the zeroth-order multipliers are just the conjugate of the respective zeroth-order parameters,

$$\bar{a}^{(0)}_u = -V^{(0)}_{0u}/G^{(0)}_{uu} = a^{(0)\dagger}_u, \tag{33}$$

$$\bar{a}^{(0)\dagger}_u = -V^{(0)}_{u0}/G^{(0)}_{uu} = a^{(0)}_u. \tag{34}$$

The Lagrange multipliers $\boldsymbol{\zeta}^{(0)}$ which correspond to the Z vector of Handy et al. [21] are determined by the equation

$$\sum_\mu \zeta^{(0)}_\mu \langle 0 | \left[\hat{E}_\mu, \left[\hat{E}_\nu, \hat{H} \right] \right] | 0 \rangle = -\gamma^{(0)}_\nu, \tag{35}$$

with

$$\gamma^{(0)}_\nu = \sum_{u \neq 0} \left(a^{(0)\dagger}_u \langle u | \left[\hat{E}_\nu, \hat{V} \right] | 0 \rangle + \langle 0 | \left[\hat{E}_\nu, \hat{V} \right] | u \rangle a^{(0)}_u \right) + \sum_{u,v \neq 0} a^{(0)\dagger}_v a^{(0)}_u \langle v | \hat{G} \left\{ \left[\hat{E}_\nu, \hat{H}^{(0)} \right] \right\} | u \rangle, \tag{36}$$

and $\hat{G}\{\hat{O}\}$ defined as $\hat{G}\{\hat{O}\} = \hat{F}\{\hat{O}\} - \langle 0 | \hat{F}\{\hat{O}\} | 0 \rangle$ where the notation $\hat{F}\{\hat{O}\}$ means that the Fock operator is calculated from the operator $\hat{O}$ instead of $\hat{H}^{(0)}$ as in (25). Introducing the one-electron density matrix [22],

$$\mathscr{D}^{(0)}_{pq} = \sum_{u,v \neq 0} \bar{a}^{(0)}_v a^{(0)}_u \left(\langle v | \hat{E}_{pq} | u \rangle - \delta_{vu} \langle 0 | \hat{E}_{pq} | 0 \rangle \right), \tag{37}$$

with the only non-vanishing elements [17]

$$\mathscr{D}^{(0)}_{ij} = -2\sum_{akb}\frac{k_{iakb}}{\Delta_{iakb}}\frac{g_{jakb}}{\Delta_{jakb}} \qquad \text{and} \qquad \mathscr{D}^{(0)}_{ab} = 2\sum_{ijc}\frac{k_{iajc}}{\Delta_{iajc}}\frac{g_{ibjc}}{\Delta_{ibjc}}, \tag{38}$$

and the generalized MP2 Fock matrix [16]

$$\phi^{(0)}_{pq} = \sum_{u\neq 0}\left(\langle 0|\sum_{\sigma}\hat{a}^{\dagger}_{p\sigma}\left[\hat{a}_{q\sigma},\hat{V}\right]|u\rangle a^{(0)}_{u} + a^{(0)\dagger}_{u}\langle u|\sum_{\sigma}\hat{a}^{\dagger}_{p\sigma}\left[\hat{a}_{q\sigma},\hat{V}\right]|0\rangle\right), \tag{39}$$

with the elements

$$\phi^{(0)}_{ip} = 2\sum_{ajb}\frac{k_{iajb}}{\Delta_{iajb}}g_{pajb} \qquad \text{and} \qquad \phi^{(0)}_{ap} = 2\sum_{ijb}\frac{k_{iajb}}{\Delta_{iajb}}g_{ipjb}, \tag{40}$$

the vector $\gamma^{(0)}$ can be calculated from the equation

$$\gamma^{(0)}_{\nu} = \left(\phi^{(0)} - \phi^{(0)\dagger}\right)_{\nu} + \sum_{pq}F\left\{\left[\hat{E}_{\nu},\hat{H}\right]\right\}_{pq}\mathscr{D}^{(0)}_{pq}. \tag{41}$$

5. The first-order responses

5.1. The MP2 multipole moments

In analogy to Eq. (3) one can define the static MP2 multipole moments as the first derivatives of the MP2 energy with respect to the field strength of an external static multipolar field

$$\Delta Q_{\mathrm{MP2}} = \left(\frac{\mathrm{d}\Delta E_{\mathrm{MP2}}}{\mathrm{d}f_{Q}(0)}\right)_{0} = \left(\frac{\partial L_{\mathrm{MP2}}}{\partial f_{Q}(0)}\right)_{0}. \tag{42}$$

By the use of the simplifications, which occur because the Lagrangian is stationary in all its variables, one obtains

$$\Delta Q_{\mathrm{MP2}} = \sum_{u,v\neq 0}a^{(0)\dagger}_{v}a^{(0)}_{u}\langle v|\hat{G}\{h^{(1)}\}|u\rangle + \sum_{\mu}\zeta^{(0)}_{\mu}\langle 0|\left[\hat{E}_{\mu},h^{(1)}\right]|0\rangle, \tag{43}$$

$$= \sum_{pq}\mathscr{D}^{(0)}_{pq}h^{(1)}_{pq} + \sum_{ai}2\left(\zeta^{(0)}_{ia}h^{(1)}_{ai} - \zeta^{(0)}_{ai}h^{(1)}_{ia}\right). \tag{44}$$

Introducing the effective density matrix

$$\rho^{(0)} = \begin{pmatrix}\mathscr{D}^{(0)}_{ij} & 2\zeta^{(0)}_{ia}\\ 2\zeta^{(0)}_{ia} & \mathscr{D}^{(0)}_{ab}\end{pmatrix}, \tag{45}$$

which is known as the relaxed [23] or variational [22] MP2 density matrix, the second-order Møller–Plesset corrections for the multipole moments can be written as

$$\Delta Q_{\mathrm{MP2}} = \sum_{pq}\rho^{(0)}_{pq}h^{(1)}_{pq}. \tag{46}$$

5.2. The first-order TDHF response equations

Expanding the TDHF equation (13) in orders of the field strengths one obtains in first order the response equation

$$\langle 0|\left[\hat{E}_\mu, \left[\hat{H}^{(0)}, \hat{\kappa}^{(1)}\right]\right]|0\rangle - \mathrm{i}\frac{\partial}{\partial t}\langle 0|\left[\hat{E}_\mu, \hat{\kappa}^{(1)}\right]|0\rangle = \langle 0|\left[\hat{E}_\mu, \hat{h}^{(1)}\right]|0\rangle. \tag{47}$$

With the Ansatz

$$\kappa_\mu^{(1)}(\omega, t) = f(+\omega)\, \mathrm{e}^{+\mathrm{i}\omega t}\kappa_\mu^{(1)}(+\omega) + f(-\omega)\, \mathrm{e}^{-\mathrm{i}\omega t}\kappa_\mu^{(1)}(-\omega) \tag{48}$$

and the matrices

$$\mathbf{A}_{\mu\nu} = \langle 0|\left[\hat{E}_\mu, \left[\hat{H}^{(0)}, \hat{E}_\nu^\dagger\right]\right]|0\rangle, \tag{49}$$

$$\mathbf{B}_{\mu\nu} = \langle 0|\left[\hat{E}_\mu, \left[\hat{E}_\nu, \hat{H}^{(0)}\right]\right]|0\rangle, \tag{50}$$

one obtains the well-known first-order TDHF response equation [3,24–27],

$$\left[\begin{pmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B} & \mathbf{A}\end{pmatrix} - 2\omega\begin{pmatrix}\mathbf{1} & \mathbf{0}\\ \mathbf{0} & -\mathbf{1}\end{pmatrix}\right]\begin{pmatrix}\kappa^{(1)}(+\omega)\\ \kappa^{(1)}(-\omega)\end{pmatrix} = -2\begin{pmatrix}h^{(1)}\\ h^{(1)}\end{pmatrix}, \tag{51}$$

5.3. The first-order response equations for the amplitudes

The expansion of Eq. (18) for the amplitudes yields in first-order in the oscillating field

$$\sum_{u\neq 0}\langle v|\left(\hat{G} - \mathrm{i}\frac{\partial}{\partial t}\right)a_u^{(1)}(\omega, t)|u\rangle = -\langle v|\left[\hat{\kappa}^{(1)}(\omega, t), \hat{V}\right]|0\rangle - \sum_{u\neq 0}a_u^{(0)}\Bigg(\langle v|\hat{G}\left\{h^{(1)}(\omega, t)\right\} + \hat{G}\left\{\left[\hat{\kappa}^{(1)}(\omega, t), \hat{H}^{(0)}\right]\right\}|u\rangle - \langle v|\hat{G}\left\{\left[\hat{\kappa}^{(1)}(\omega, t), \mathrm{i}\frac{\partial}{\partial t}\right]\right\}|u\rangle\Bigg), \tag{52}$$

where

$$\hat{J}^{(1)}(\omega, t) = \hat{h}^{(1)}(\omega, t) + \left[\hat{\kappa}^{(1)}(\omega, t), \hat{H}^{(0)}\right] \tag{53}$$

is an effective Hamiltonian for the first order in the external field. The matrix elements

$$\langle v|\hat{G}\left\{\left[\hat{\kappa}^{(1)}(\omega, t), \mathrm{i}\frac{\partial}{\partial t}\right]\right\}|u\rangle = -\mathrm{i}\sum_{pq}\kappa_{pq}^{(1)}(\omega, t)\left(\langle v|\hat{E}_{pq}|u\rangle - \delta_{vu}\langle 0|\hat{E}_{pq}|0\rangle\right) \tag{54}$$

vanish, because we do not use the redundant occupied–occupied and virtual–virtual rotations. With the Ansatz

$$a_u^{(1)}(\omega, t) = f(\omega)\, \mathrm{e}^{\mathrm{i}\omega t}a_u^{(1)}(\omega) + f(-\omega)\, \mathrm{e}^{-\mathrm{i}\omega t}a_u^{(1)}(-\omega) \tag{55}$$

and the abbreviations

$$V_{vu}^{(1)}(\omega) = \langle v|\left[\hat{\kappa}^{(1)}(\omega), \hat{V}\right]|u\rangle \quad \text{and} \quad G_{vu}^{(1)}(\omega) = \langle v|\hat{G}\left\{\hat{J}^{(1)}(\omega)\right\}|u\rangle, \tag{56}$$

we find the equation

$$\sum_{u\neq 0}\left(G_{vu}^{(0)} + \omega\right)a_u^{(1)}(\omega) = -V_{v0}^{(1)}(\omega) - \sum_{u\neq 0}G_{vu}^{(1)}(\omega)\, a_u^{(0)}, \tag{57}$$

which can be solved immediately, because the matrix $\mathbf{G}^{(0)}$ is diagonal,

$$a_u^{(1)}(\omega) = +\frac{V_{u0}^{(1)}(\omega)}{\Delta_u - \omega} + \frac{G_{uv}^{(1)}(\omega) V_{v0}^{(0)}}{(\Delta_u - \omega)\Delta_v}, \tag{58}$$

Proceeding in the same way as above, one obtains for the conjugated first-order amplitudes

$$a_u^{(1)}(\omega)^\dagger = +\frac{V_{0u}^{(1)}(\omega)}{\Delta_u + \omega} + \frac{V_{0v}^{(0)} G_{vu}^{(1)}(\omega)}{\Delta_v(\Delta_u + \omega)}. \tag{59}$$

6. The calculation of the dynamic polarizabilities

If one applies the variational conditions for the MP2 energy Lagrangian and the first-order response equations for the parameters $\boldsymbol{\kappa}^{(1)}$, $\boldsymbol{a}^{(1)}$ and $\boldsymbol{a}^{(1)\dagger}$ in the calculation of the second derivatives, one obtains an expression, which in accordance with the $2n+1$ rule and the $2n+2$ rule [15,17] for the parameters and their multipliers, respectively, does not contain second derivatives of the parameters or any derivatives of the multipliers,

$$\begin{aligned}
&\Delta\alpha_{\mathrm{MP2}}(-\omega;+\omega) \\
&= \mathrm{Re}\sum_{v,u\neq 0} a_v^{(0)\dagger}\left[\langle v|\hat{G}\{\hat{J}^{(1)}(+\omega)\}|u\rangle a_u^{(1)}(-\omega) + \langle v|\hat{G}\{\hat{J}^{(1)}(-\omega)\}|u\rangle a_u^{(1)}(+\omega)\right] \\
&\quad + \mathrm{Re}\sum_{u\neq 0}\left(\langle 0|\left[\hat{\kappa}^{(1)}(+\omega), \hat{V}\right]|u\rangle a_u^{(1)}(-\omega) + \langle 0|\left[\hat{\kappa}^{(1)}(-\omega), \hat{V}\right]|u\rangle a_u^{(1)}(+\omega)\right) \\
&\quad + 2\sum_{u\neq 0}\langle 0|\left[\hat{\kappa}^{(1)}(+\omega), \hat{\kappa}^{(1)}(-\omega), \hat{V}\right]|u\rangle a_u^{(0)} \\
&\quad + \sum_{v,u\neq 0} a_v^{(0)\dagger} a_u^{(0)}\langle v|\hat{G}\{\hat{J}^{(2)}(+\omega,-\omega) + \omega[\hat{\kappa}^{(1)}(+\omega), \hat{\kappa}^{(1)}(-\omega)]\}|u\rangle \\
&\quad + \langle 0|\left[\hat{\zeta}^{(0)}, \hat{J}^{(2)}(\omega,-\omega) + \omega[\hat{\kappa}^{(1)}(\omega), \hat{\kappa}^{(1)}(-\omega)]\right]|0\rangle,
\end{aligned} \tag{60}$$

where $\hat{J}^{(2)}(+\omega,-\omega)$ is an effective Hamiltonian for the second order in the external field

$$\begin{aligned}
&\hat{J}^{(2)}(+\omega,-\omega) \\
&= \left[\hat{\kappa}^{(1)}(+\omega), \hat{h}^{(1)}(-\omega)\right] + \left[\hat{\kappa}^{(1)}(-\omega), \hat{h}^{(1)}(+\omega)\right] + \left[\hat{\kappa}^{(1)}(-\omega), \hat{\kappa}^{(1)}(+\omega), \hat{H}^{(0)}\right].
\end{aligned} \tag{61}$$

The first two terms contributing to $\Delta\alpha_{\mathrm{MP2}}(-\omega,+\omega)$ can be calculated as an MP2 energy with modified integrals and frequency-dependent energy denominators,

$$\begin{aligned}
&\mathrm{Re}\Bigg(\sum_{v,u\neq 0} a_v^{(0)\dagger} a_u^{(1)}(-\omega)\langle v|\hat{G}\{\hat{J}^{(1)}(+\omega)\}|u\rangle \\
&\quad + \sum_{u\neq 0}\langle 0|\left[\hat{\kappa}^{(1)}(+\omega), \hat{V}\right]|u\rangle a_u^{(1)}(-\omega) + (+\omega \leftrightarrow -\omega)\Bigg) \\
&= \mathrm{Re}\sum_u\left(\frac{I_{0u}^{(1)}(+\omega) I_{u0}^{(1)}(-\omega)}{\Delta_u - \omega} + \frac{I_{0u}^{(1)}(-\omega) I_{u0}^{(1)}(+\omega)}{\Delta_u + \omega}\right),
\end{aligned}$$

with

$$I^{(1)}_{u0}(\omega) = V^{(1)}_{u0}(\omega) + \sum_v G^{(1)}_{uv}(\omega)\frac{V^{(0)}_{v0}}{\Delta_v}, \tag{63}$$

$$I^{(1)}_{0u}(\omega) = V^{(1)}_{0u}(\omega) + \sum_v \frac{V^{(0)}_{0v}}{\Delta_v} G^{(1)}_{vu}(\omega). \tag{64}$$

The third term is an MP2 energy calculated from two-index transformed integrals and zeroth-order amplitudes,

$$2\sum_{u\neq 0}\langle 0|\left[\hat{\kappa}^{(1)}(+\omega),\ \hat{\kappa}^{(1)}(-\omega),\ \hat{V}\right]|u\rangle a^{(0)}_u$$

$$= \sum_{iajb}\left\{\kappa^{(1)}(+\omega),\left\{\kappa^{(1)}(-\omega),\ g\right\}\right\}_{iajb}\frac{k_{iajb}}{\Delta_{iajb}} + (+\omega \leftrightarrow -\omega). \tag{65}$$

The last two terms can be calculated with the effective density matrix $\boldsymbol{\rho}^{(0)}$,

$$\sum_{v,u\neq 0} a^{(0)\dagger}a^{(0)}_u\langle v|\hat{G}\left\{\hat{J}^{(2)}(+\omega,-\omega) + \omega\left[\hat{\kappa}^{(1)}(+\omega),\ \hat{\kappa}^{(1)}(-\omega)\right]\right\}|u\rangle$$

$$+\langle 0|\left[\hat{\zeta}^{(0)},\ \hat{J}^{(2)}(+\omega,-\omega) + \omega\left[\hat{\kappa}^{(1)}(+\omega),\ \hat{\kappa}^{(1)}(-\omega)\right]\right]|0\rangle$$

$$= \sum_{pq}\rho^{(0)}_{pq}\left[F\left\{\hat{J}^{(2)}(+\omega,-\omega)\right\}_{pq} + \omega\left\{\kappa^{(1)}(+\omega),\ \kappa^{(1)}(-\omega)\right\}_{pq}\right]. \tag{66}$$

7. First applications to helium and neon

In order to test our method and its implementation, we computed frequency-dependent polarizabilities for the rare-gas atoms helium and neon, for which experimental and theoretical data are available. For both atoms we used large basis sets which are expected to give dipole and quadrupole polarizabilities near the basis set limits and have been used previously for calculations in the framework of SDT-MBPT [4,9,28], so that a direct comparison between the two methods is possible. For helium we used the uncontracted (10s5p3d2f) basis set optimized for polarizability calculations by Meyer [29], and for neon we used the (19s14p5d3f3g)/[12s10p5d3f3g] contracted basis given by Thakkar et al. [28]. The results for the static dipole, quadrupole and octupole polarizabilities for helium and neon as well as the isotropic C_6, C_8 and C_{10} dispersion coefficients for

Table 1
Static dipole, quadrupole and octupole polarizabilities for He and C_6, C_8 and C_{10} coefficients for $(He)_2$ (in au)

	TDHF [a]	TDMP2 [b]	MBPT [c]	FCI [d]
α_1	1.322	1.362	1.354	1.385
α_2	2.315	2.403	2.372	2.445
α_3	9.940	10.37	10.22	10.60
C_6	1.375	1.430	1.431	1.463
C_8	13.12	13.76	13.66	14.11
C_{10}	168.4	178.0	175.8	183.2

[a] Time-dependent Hartree–Fock (this work).
[b] Time-dependent Møller-Plesset second order (this work).
[c] Many-Body perturbation theory [4].
[d] Full-CI [30].

Table 2
C_6, C_8 and C_{10} coefficients for He–Ne (in au)

	TDHF [a]	TDMP2 [b]	MBPT [c]	DOSD [d]
C_6	2.727	3.041	3.071	3.029
C_8	31.36	36.12	36.18	
C_{10}	453.5	548.9	545.1	

[a] Time-dependent Hartree–Fock (this work).
[b] Time-dependent Møller–Plesset second order (this work).
[c] Many-body perturbation theory [28].
[e] Dipole oscillator strength distribution [31].

Table 3
Static dipole, quadrupole and octupole polarizabilities for Ne and C_6, C_8 and C_{10} coefficients for $(Ne)_2$ (in au)

	TDHF [a]	TDMP2 [b]	MBPT [c]	CCSD(T) [d]	DOSD [e]
α_1	2.375	2.720	2.656	2.69	2.669
α_2	6.401	7.651	7.328	7.52	
α_3	34.12	44.94	42.07		
C_6	5.514	6.543	6.553		6.383
C_8	73.46	91.79	90.344		
C_{10}	1177.1	1589.4	1535.6		

[a] Time-dependent Hartree–Fock (this work).
[b] Time-dependent Möller–Plesset second order (this work).
[c] Many-body perturbation theory [28].
[d] Ref. [32].
[e] Dipole oscillator strength distribution [31].

the van der Waals systems He_2, He–Ne and Ne_2 are given in Tables 1–3. In Fig. 1 we compare the dynamic polarizabilities for neon at imaginary frequencies obtained from the time-dependent MP2 (TDMP2) method with the TDHF results and values calculated from a effective dipole oscillator strength distribution (DOSD) determined from experimental data by Kumar and Meath [31]. For polarizabilities as well as the dispersion coefficients we obtain results which differ not more than 3% from the best experimental or theoretical data. In comparison with the SDT-MBPT method, time-dependent MP2 yields with the same basis sets slightly larger results for static polarizabilities.

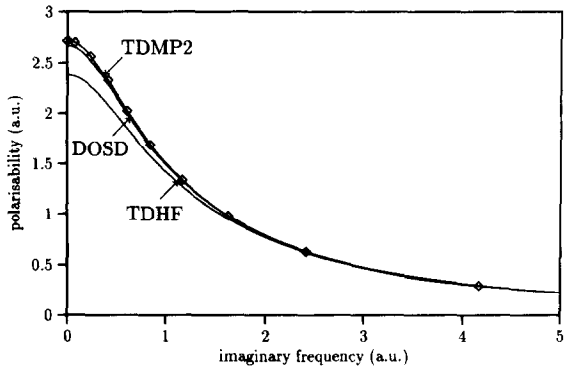


Fig. 1. Dipole polarizability of neon at imaginary frequencies.

Acknowledgement

We wish to thank Paul E.S. Wormer and Jeppe Olsen for helpful discussions. This work has been funded by the Deutsche Forschungsgemeinschaft through the Sonderforschungsbereich 334. We also acknowledge support by the Fonds der Chemischen Industrie.

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