On the finite-field transition dipole moment calculations by effective Hamiltonian methods

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Abstract. A simple finite-field scheme of calculations on electronic transition dipole moments in molecules by effective Hamiltonian methods is presented and discussed. The reliability of underlying approximations is analyzed by means of the quasidegenerate perturbation theory and corroborated by the results of pilot numerical applications.

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1 Introduction

The finite-field (FF) technique [1,2] is recognized to be a valuable tool for theoretical evaluation of molecular properties other than the energy. Numerous studies [3–5] have demonstrated its capability to provide highly accurate electric multipole moments and polarizabilities of molecules in pure electronic states. A straightforward generalization of the FF approach to the description of transition properties [6,7] allows to use it in theoretical studies of spectral intensities and radiative lifetimes of excited electronic states. As has been recently shown [7], the finite-field transition dipole moment (TDM) estimates are normally less sensitive to the level of correlation treatment than directly computed off-diagonal electric dipole matrix elements between the initial and final states.

Finite-field TDM estimates are derived from the response of electronic wavefunctions to a perturbation by external uniform electric field, and the computational scheme of the method implies the construction of approximate wavefunctions for several values of field intensity. At the same time popular procedures of correlation electronic structure calculations based on the effective Hamiltonian theory ([8,9] and references therein) usually avoid the explicit construction of total approximate electronic wavefunctions and provide, along with energy values, only so-called model wavefunctions, *i.e.* the projections of total wavefunctions onto a given subspace of the total functional space (model space).

The present paper formulates and examines an elementary approach to FF transition moment calculations within the framework of effective Hamiltonian theory, based on the analysis of the response of model wavefunctions to an external perturbation. For the sake of simplicity we restrict our attention to the case of fixed (field-independent) model spaces; it should be noted, however, that our approach can be naturally combined with the field-dependent optimization of model spaces.

Section 2 provides a brief outline of the FF method for transition moment calculations. In the next section we analyze the off-diagonal Hellmann-Feynman-like relation for effective Hamiltonian eigenstates which provides the theoretical basis for the present approach. The reliability of model-space FF transition moment estimates is discussed in Section 4. The last section contains the concluding remarks.

2 Finite-field method for transition moment calculations

The FF method derives the estimate for transition dipole moment D_{if} between two stationary electronic states $|\psi_i\rangle$, $|\psi_f\rangle$ from the response of these states to a perturbation by an external uniform electric field. Let us recall the main points of this approach. The dependence of the molecular electronic Hamiltonian H on the external field intensity F is given by the formula

$$H(F) = h - DF, \qquad (1)$$

where $D = -(\partial H/\partial F)$ is the electric dipole operator and $h \equiv H(0)$ stands for the Hamiltonian of the free molecule. The exact F-dependent eigenfunctions $|\psi_i\rangle$, $|\psi_f\rangle$, and the eigenvalues E_i, E_f of (1) should satisfy the off-diagonal Hellmann-Feynman theorem

$$\langle\Psi_i|D|\Psi_f\rangle = (E_i - E_f)\langle\Psi_i|\frac{\partial}{\partial F}\Psi_f\rangle|_{F=0}. \qquad (2)$$

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In what follows we shall restrict our attention to small field intensities and the symbol $|_{F=0}$ will be omitted. The FF transition dipole moment estimate is given by the finite-difference approximation for the r.h.s. of equation (2):

$$(D_{if}^{FF})_\eta = (E_i - E_f) \lim_{\substack{F_\eta \to 0 \\ F_{\eta' \neq \eta} = 0}} \left(\frac{\langle \Psi_i(-F_\eta/2)|\Psi_f(F_\eta/2)\rangle}{F_\eta} \right),$$

$$\eta = x, y, z. \tag{3}$$

For approximate eigenstates resulted from practical *ab initio* calculations, D_{if}^{FF} can differ from the corresponding off-diagonal dipole matrix element $\langle \Psi_i|D|\Psi_f\rangle$ (dipole length form of transition moment, or D_{if}^{DL}). Nevertheless one easily verifies that the relations (1–2) are still valid for approximate wavefunctions obtained by diagonalizing $H(F)$ within a fixed (F-independent) subspace of the total Hilbert space. This implies the strict equivalence of the finite-field and dipole length transition moment estimates by variational configuration expansion methods provided that the same MO set is employed for calculations with different F values. Independent optimization of molecular orbitals for each field intensity destroys this equivalence, and the use of D_{if}^{FF} which incorporate MO relaxation effects appears to be *a priori* preferable [7]. As we shall see later, D_{if}^{FF} should also differ from D_{if}^{DL} when the eigenstates of H are approximated by the corresponding eigenstates of an effective Hamiltonian.

3 Hellmann-Feynman-like relation for model eigenstates

Let us divide the total functional space L into a model space L_P with its projector P and an outer space L_Q projected by $Q = 1 - P$. We shall assume that this partitioning does not depend on the field intensity F. An effective Hamiltonian $\tilde{H}$ acting within L_P and having the eigenvalues identical to (dim L_P) eigenenergies of H

$$\tilde{H}|\tilde{\Psi}_j\rangle = E_j|\tilde{\Psi}_j\rangle \tag{4}$$

should satisfy the generalized Bloch equations [10]

$$H\Omega = \Omega\tilde{H}. \tag{5}$$

Here $\Omega = \Omega P$ is the (right) wave operator which transforms the right eigenvectors of $\tilde{H}$ into the target eigenvectors of the total Hamiltonian:

$$\Omega|\tilde{\Psi}_j\rangle = |\Psi_j\rangle. \tag{6}$$

It is convenient to introduce the left wave operator $\Omega^{\perp\perp}$ [11,12] which effects the inverse mapping:

$$\Omega^{\perp\perp}\Omega = P, \tag{7}$$

$$\Omega\Omega^{\perp\perp} = \sum_{j=1}^{\dim L_P} |\Psi_j\rangle\langle\Psi_j|. \tag{8}$$

The effective Hamiltonian is given in terms of the wave operators by the equation

$$\tilde{H} = \Omega^{\perp\perp}H\Omega. \tag{9}$$

Note that $\tilde{H}$ is generally non-Hermitian and its left eigenvectors $\{|\tilde{\Psi}_j^{\perp\perp}\rangle\}$ differ from $\{|\tilde{\Psi}_j\rangle\}$. The right and left eigenvectors are biorthogonal and we can normalize $\{|\tilde{\Psi}_j^{\perp\perp}\rangle\}$ by the conditions

$$\langle\tilde{\Psi}_j^{\perp\perp}|\tilde{\Psi}_k\rangle = \delta_{jk}, \tag{10}$$

i.e. in such a way that

$$\langle\tilde{\Psi}_j^{\perp\perp}|\tilde{H}|\tilde{\Psi}_k\rangle = \delta_{jk}E_j. \tag{11}$$

Provided that equations (4–5) are solved, one can in principle obtain transition dipole moment values *via* calculating the total electronic wavefunctions $|\tilde{\Psi}_j\rangle$, $|\tilde{\Psi}_f\rangle$ by means of the wave operator (see Eq. (6)). However, explicit construction of the wavefunctions and even the storage of the wave operator usually appear to be incompatible with the computational efficiency. Within the dipole length representation the problem is naturally solved by introducing the effective electric dipole operator $\tilde{D}$ acting upon L_P [12–14]. We shall adopt the definition of effective operators given in [12]:

$$\tilde{D} = \Omega^{\perp\perp}D\Omega. \tag{12}$$

Using (12), one can express transition dipole moments entirely in terms of model-space entities since

$$\langle\Psi_i|D|\Psi_f\rangle = \langle\tilde{\Psi}_i^{\perp\perp}|\tilde{D}|\tilde{\Psi}_f\rangle. \tag{13}$$

To adapt the FF technique to the framework of effective Hamiltonian theory, one might try to relate the matrix element (13) directly to the response of model wavefunctions to the external perturbation. Differentiating equations (10, 11) with respect to the electric field intensity, one readily arrives at a Hellmann-Feynman-like relation

$$-\langle\tilde{\Psi}_i^{\perp\perp}|\frac{\partial\tilde{H}}{\partial F}|\tilde{\Psi}_f\rangle = (E_i - E_f)\langle\tilde{\Psi}_i^{\perp\perp}|\frac{\partial}{\partial F}\tilde{\Psi}_f\rangle. \tag{14}$$

The r.h.s. of equation (14) is formally similar to that of equation (2) and may be evaluated by a finite-difference scheme. The resulting value which we shall denote by $\mathbf{D}_{if}^{FF}$ is the FF TDM estimate provided that the model wavefunctions are considered as approximations for total wavefunctions. This estimate is obviously not exact since $-\partial\tilde{H}/\partial F$ does not coincide with the effective dipole operator (12). To find the relation connecting these two operators, let us differentiate equation (9) with respect to F:

$$\frac{\partial\tilde{H}}{\partial F} = -\tilde{D} + \frac{\partial\Omega^{\perp\perp}}{\partial F}H\Omega + \Omega^{\perp\perp}H\frac{\partial\Omega}{\partial F}. \tag{15}$$

Making use of the Bloch equation (5), its "left" counterpart

$$\tilde{H}\Omega^{\perp\perp} = \Omega^{\perp\perp}H. \tag{16}$$

and taking into account the differential form of equation (7), one can transform equation (15) to

$$\frac{\partial \tilde{H}}{\partial F} = -\tilde{D} - \left[\Omega^{\perp\perp}\frac{\partial \Omega}{\partial F}, \tilde{H}\right]. \qquad (17)$$

The deviations of the model-space FF transition moment estimates from corresponding exact values arise from the presence of commutator in the r.h.s. of equation (17):

$$\mathbf{D}_{if}^{FF} - D_{if} = \langle \tilde{\Psi}_i^{\perp\perp}|[\Omega^{\perp\perp}\frac{\partial \Omega}{\partial F}, \tilde{H}]|\tilde{\Psi}_f\rangle$$

$$= (E_f - E_i)\langle \tilde{\Psi}_i^{\perp\perp}|\Omega^{\perp\perp}\frac{\partial \Omega}{\partial F}|\tilde{\Psi})_f\rangle. \qquad (18)$$

4 Perturbative analysis and numerical illustrations

In order to evaluate the reliability of the model-space FF transition moment estimates $\mathbf{D}_{if}^{FF}$ we shall analyze the deviation of $-\partial \tilde{H}/\partial F$ from $\tilde{D}$ by means of the quaside-generate perturbation theory (QDPT). Suppose that the free-molecule Hamiltonian h is split into a zero-order part h_0 and a perturbation v in such a way that

$$h_0 P = P h_0 \qquad (19)$$

and the exact eigensolutions of the zero-order problem

$$h_0|k\rangle = \varepsilon_k|k\rangle \qquad (20)$$

are available. This splitting naturally induces a similar partitioning of the Hamiltonian (1):

$$H(F) = h_0 + V, \; V = v - DF. \qquad (21)$$

Now we can expand the effective operators in powers of V and compare $-\partial \tilde{H}/\partial F$ and $\tilde{D}$ order by order at $F = 0$. Explicit formulas for effective Hamiltonian expansions can be found elsewhere [10,15,16]. The expansions for effective property operators are readily derived from well-known QDPT series for wave operators [10–15]. If we adopt the intermediate normalization

$$P\Omega = P, \quad \text{or} \quad |\tilde{\Psi}_j\rangle = P|\Psi_j\rangle, \qquad (22)$$

the first terms in the $\tilde{D}$ expansion are given by

$$\tilde{D}^{(0)} = PDP,$$

$$\tilde{D}^{(1)} = \Omega^{(1)\dagger}DP + PD\Omega^{(1)},$$

$$\tilde{D}^{(2)} = \Omega^{(2)\dagger}DP + PD\Omega^{(2)} + \Omega^{(1)\dagger}D\Omega^{(1)}$$

$$- \Omega^{(1)\dagger}\Omega^{(1)}DP \quad etc. \qquad (23)$$

Since V is a linear function of the field intensity and $\partial \tilde{H}^{(q)}/\partial F = (\partial \tilde{H}/\partial F)^{(q-1)}$, the derivative of the qth order effective Hamiltonian should be compared with

$\tilde{D}^{(q-1)}$. Let us begin with noting that $\tilde{H}^{(0\div 1)} \equiv \tilde{H}^{(0)} + \tilde{H}^{(1)} = PHP$ and

$$-\frac{\partial \tilde{H}^{(0\div 1)}}{\partial F} = PDP = \tilde{D}^{(0)}. \qquad (24)$$

Equation (24) reflects the well-known fact that the off-diagonal Hellmann-Feynman theorem (2) holds for approximate eigenstates obtained by diagonalizing the Hamiltonian within any fixed subspace (cf. [17]). The second-order correction to the effective Hamiltonian is expressed by the formula

$$\tilde{H}^{(2)} = \sum_{mn}\sum_a |m\rangle\frac{H_{ma}H_{an}}{\Delta_{na}}\langle n| \qquad (25)$$

where the indices $m, n, \cdots$ and $a, b, \cdots$ are used for model-space and outer-space zero-order solutions respectively, $\Delta_{na} \equiv \varepsilon_n - \varepsilon_a$ and $H_{ma} = \langle m|H|a\rangle = \langle m|V|a\rangle$ (we suppose that these matrix elements are real). The derivative of (25) at $F = 0$ is given by

$$-\frac{\partial \tilde{H}^{(2)}}{\partial F} = \sum_{mn}\sum_a |m\rangle\frac{D_{ma}h_{an} + h_{ma}D_{an}}{\Delta_{na}}\langle n|. \qquad (26)$$

One easily notes that (26) resembles the well-known expression for $\tilde{D}^{(1)}$:

$$\tilde{D}^{(1)} = \sum_{mn}\sum_a |m\rangle\left(\frac{D_{ma}h_{an}}{\Delta_{na}} + \frac{h_{ma}D_{an}}{\Delta_{ma}}\right)\langle n|. \qquad (27)$$

Provided that h_0 is strictly degenerate within the model space ($\varepsilon_m = \varepsilon_n = \cdots = \varepsilon_0$), the r.h.s. of equations (26, 27) coincide and

$$-\frac{\partial \tilde{H}^{(2)}}{\partial F} = \tilde{D}^{(1)}. \qquad (28)$$

In this case the difference between the order-by-order expansions of $-\partial \tilde{H}/\partial F$ and $\tilde{D}$ first appears only at the second order (third order for $\tilde{H}$) and comprises "renormalization-like" terms:

$$-\frac{\partial \tilde{H}^{(3)}}{\partial F} = \tilde{D}^{(2)} + \sum_{mn}|m\rangle G_{mn}\langle n|,$$

$$G_{mn} = \sum_{m'a}(v_{mm'}h_{m'a}D_{an} - h_{ma}D_{am'}v_{m'n})\Delta_a^{-2}$$

$$= \sum_{\substack{m':\\m'\neq m\\m'\neq n}}\sum_a (h_{mm'}h_{m'a}D_{an} - h_{ma}D_{am'}h_{m'n}\Delta_a^{-2}$$

$$+ \sum_a (h_{ma}D_{an}(h_{mn} - h_{nn})$$

$$- h_{mn}(h_{ma}D_{am} - h_{na}D_{an}))\Delta_a^{-2},$$

$$\Delta_a = \varepsilon_0 - \varepsilon_a. \qquad (29)$$

For non-degenerate cases equation (28) does not hold; however, provided that

$$|\Delta_{na} - \Delta_{ma}| \ll |\Delta_{na}| \qquad (30)$$

for all m, n, a: $|m\rangle, |n\rangle \in L_P$, $|a\rangle \in L_Q$, the operator (26) should still reasonably fit the first-order correction for the effective dipole operator and therefore

$$\mathbf{D}_{if}^{FF} \cong \langle \tilde{\Psi}_i^{\perp\perp} | \tilde{D}^{(0\div 1)} | \tilde{\Psi}_f \rangle. \tag{31}$$

Moreover, the approximate relation (31) remains valid even when the requirement (30) is fulfilled only for the model-space vectors $|m\rangle$, $|n\rangle$ with large weights in the target model functions $|\tilde{\Psi}_i\rangle$, $|\tilde{\Psi}_f\rangle$, and the outer-space vectors $|a\rangle$ strongly coupled to the model space. Equations (28, 31) indicate that the FF transition dipole moments $\mathbf{D}_{if}^{FF}$ computed with the model-space functions $|\tilde{\Psi}_i\rangle$, $|\tilde{\Psi}_f\rangle$, comprise the bulk of first-order contributions to TDM values from outer-space vectors. In contrast, if one uses the same functions as approximate wavefunctions for direct computation of transition matrix element $\mathbf{D}_{if}^{DL} = \langle \tilde{\Psi}_i^{\perp\perp} | D | \tilde{\Psi}_f \rangle = \langle \tilde{\Psi}_i^{\perp\perp} | \tilde{D}^{(0)} | \tilde{\Psi}_f \rangle$, such contributions will be lost.

Similar conclusions can be drawn from the analysis of various types of effective operators. Let us first notice that the particular choice of normalization (22) is not of importance. For instance, in passing to the isometry normalization conditions [18], one arrives at the following expressions for the Hermitian second-order effective Hamiltonian [15] and its derivative:

$$\tilde{H}^{(2)} = \frac{1}{2} \sum_{mn} \sum_a |m\rangle H_{ma}(\Delta_{ma}^{-1} + \Delta_{na}^{-1}) H_{an} \langle n| \tag{32}$$

$$-\frac{\partial \tilde{H}^2}{\partial F} = \frac{1}{2} \sum_{mn} \sum_a |m\rangle (D_{ma} h_{an} + h_{ma} D_{an}) \\ \times (\Delta_{ma}^{-1} + \Delta_{na}^{-1}) \langle n| \tag{33}$$

while the first-order effective dipole operator is still given by the formula (27). The comparison of equations (27, 33) immediately leads to (31) under the same conditions. It is noteworthy that the Hermiticity of $\tilde{H}$ and its derivative resulting from the choice of the isometric normalization guarantees that $\mathbf{D}_{if}^{DL} = \mathbf{D}_{fi}^{DL}$, while the use of the normalization (22) gives rise to a spurious difference between $i \to f$ and $f \to i$ FF TDM values. Furthermore, the formulas (25, 27) (or (33, 27)) with somewhat different definitions of energy denominators yield second-order state-specific Hamiltonians and corresponding first-order effective property operators appearing in the intermediate-Hamiltonian QDPT [8,19,20] or multipartitioning perturbation theory (MPPT) [21], and the argumentation given above is also applicable to these cases.

With an appropriate choice of model spaces, effective Hamiltonian methods take advantage from the inhomogeneity of electron correlation effects [22]. The nondynamic (internal, left-right) correlations are associated with the interaction of model-space configurations while the dynamic correlations arise from the coupling between the model and outer spaces. It is convenient to distinguish the "direct" dynamic (outer-space) contributions to a property under study and interference effects resulting

Table 1. Transition dipole moments for the vertical excitations $X^1 A_g \to 1, 2^1 B_{1u}$ of the ethylene molecule, a.u.

Model space	Method	$X^1 A_g \to 1^1 B_{1u}$		$X^1 A_g \to 2^1 B_{1u}$	
		$\mathbf{D}_{if}^{DL}$	$\mathbf{D}_{if}^{FF}$	$\mathbf{D}_{if}^{DL}$	$\mathbf{D}_{if}^{FF}$
val-π[a]	model space CI	0.962		0.738	
	DPT/2	1.604	1.430	0.395	0.325
	MPPT/2	1.539	1.389	0.415	0.346
full-π[b]	model space CI	1.122		0.750	
	MPPT/2	1.559	1.349	0.453	0.378
full-2el[c]	model space CI	1.186		0.736	
	MPPT/2	1.565	1.358	0.451	0.377
	DDCI[d]	1.351		0.365	
	MRCI [28]	1.33			

Active MO spaces comprised, [a] eight lowest-energy valence-and Rydberg-like π-MO, [b] all the π-MO, [c] all MO's except for those of doubly-occupied σ-shell. [d] The DDCI calculations were performed using the model space $(val-\pi)$ as the reference space.

from the influence of $L_P - L_Q$ couplings on the model-space part of the wavefunctions *via* the effective interactions [22]. If we evaluate the TDM from the PHP eigenstates, the dynamic correlations are completely ignored. The $\mathbf{D}_{if}^{DL}$ values computed with the model wavefunctions take into account the interference effects but the direct dynamic contributions are still neglected. Equation (31) shows that the $\mathbf{D}_{if}^{FF}$ estimates should incorporate, along with the interference effects, essential direct effects of dynamic correlations.

Let us consider a simple numerical illustration. The lowest $^1 B_{1u}$ states of the ethylene molecule provide a well-known example of strong interferences between $\pi - \pi$ (nondynamic) and $\sigma - \pi$ (dynamic) correlations. While the $X \to 1, 2^1 B_{1u}$ transitions can be described essentially in terms of $\pi \to \pi$-substitutions, a proper description of the $\sigma - \pi$-correlations is of crucial importance for reproducing the valence-like nature of the $1^1 B_{1u}(V)$ state (see [20] and references therein for a detailed discussion). Our effective Hamiltonian calculations on the vertical $X \to 1, 2^1 B_{1u}$ transitions of ethylene were performed with three different complete model spaces arising from all the possible distributions of two "π" electrons among the active orbitals (see Tab. 1); in all cases, the $\sigma - \pi$-correlations were associated with the $L_P - L_Q$ coupling. The employed basis set comprised the atomic contracted Gaussian bases $(5s3p2d)$ C [23], $(3s1p)$ H [24] and primitive diffuse Gaussians $(2p2d)$ on the molecular center of masses. A fixed (field-independent) MO set ensuring a roughly balanced description of valence-like and Rydberg states was generated by solving the fractional-occupancy SCF equations for the field-free $(C_2H_4)^{+0.5}$ problem. Hermitian effective Hamiltonians were constructed by the second-order many-body MPPT method (MPPT/2) [21], employing the diagrammatic algorithm [25]; for the smallest model

space we also used the degenerate perturbation theory (DPT/2) with "forced degeneracy" of active orbital energies [26]. For the sake of comparison we carried out extensive difference-dedicated CI (DDCI) [27] calculations with the same orbital basis set. Let us remind that the dipole-length and finite-field CI TDM values should coincide since the MO's (and therefore the variational CI spaces) do not depend on the field intensity (*cf.* Sect. 2).

The results are listed in Table 1. In all cases the TDM estimates derived from the model-space (two-electron CI) problem are rather poor because of the complete neglect of $\sigma-\pi$-correlations. In passing to the eigenstates of the effective Hamiltonians the computed TDM change dramatically. One should notice that the proper account for the correlation interference effects in the off-diagonal dipole matrix element ($\mathbf{D}_{if}^{DL}$) calculations is necessary but obviously not sufficient for obtaining accurate TDM values, and only the incorporation of the direct contributions from the $\sigma-\pi$-excitations by means of the FF technique ensures a good agreement with the results of extensive CI treatment. Finally let us try to predict the general trends in accuracy of the method proposed above. Provided that the perturbation v is rather small, the basic requirement (30) is hardly fulfilled even for the vectors $|m\rangle, |n\rangle$ dominating the initial and final states when $|E_i - E_f|$ is large. The uselessness of any attempt to bypass this difficulty by introducing an additional diagonal "degeneracy-forcing" perturbation is illustrated by the presence of the terms proportional to $h_{mm} - h_{nn}$ in equation (29). As a consequence, one might expect that the accuracy of our FF results will decrease with the increase of transition energies.

The results of our test MPPT/2 calculations on transition dipole moments for the benchmark system CH^+ seem to corroborate this hypothesis. To enable the comparison with the full CI data of Olsen *et al.* [24] we employed the same basis set and fixed the internuclear distance at 2.13713 a.u. Field-free molecular orbitals from the ground-state SCF calculations on CH^{2+} were used. A series of model spaces of increasing size was constructed by the numerical selection of large-weight Slater determinants. The deviations of obtained $\mathbf{D}_{if}^{DL}$ and $\mathbf{D}_{if}^{FF}$ values from the corresponding full-CI TDM are plotted in Figure 1. For the lowest-energy transition the convergence of the $\mathbf{D}_{if}^{FF}$ values to the full-CI one with the extension of the model space is much faster than that for $\mathbf{D}_{if}^{DL}$'s due to an accurate estimation of direct outer-space contributions by the FF scheme. For higher-energy transitions the difference of convergence rates is not so large; this is readily explained by a relatively low accuracy of the approximation (31).

5 Conclusions

A straightforward adaptation of the finite-field technique to the calculations on electronic transition dipole moments by effective Hamiltonian methods is presented. Approximate transition moments are derived from the response of the effective Hamiltonian eigenvectors to the perturbation by a small uniform electric field. Although these
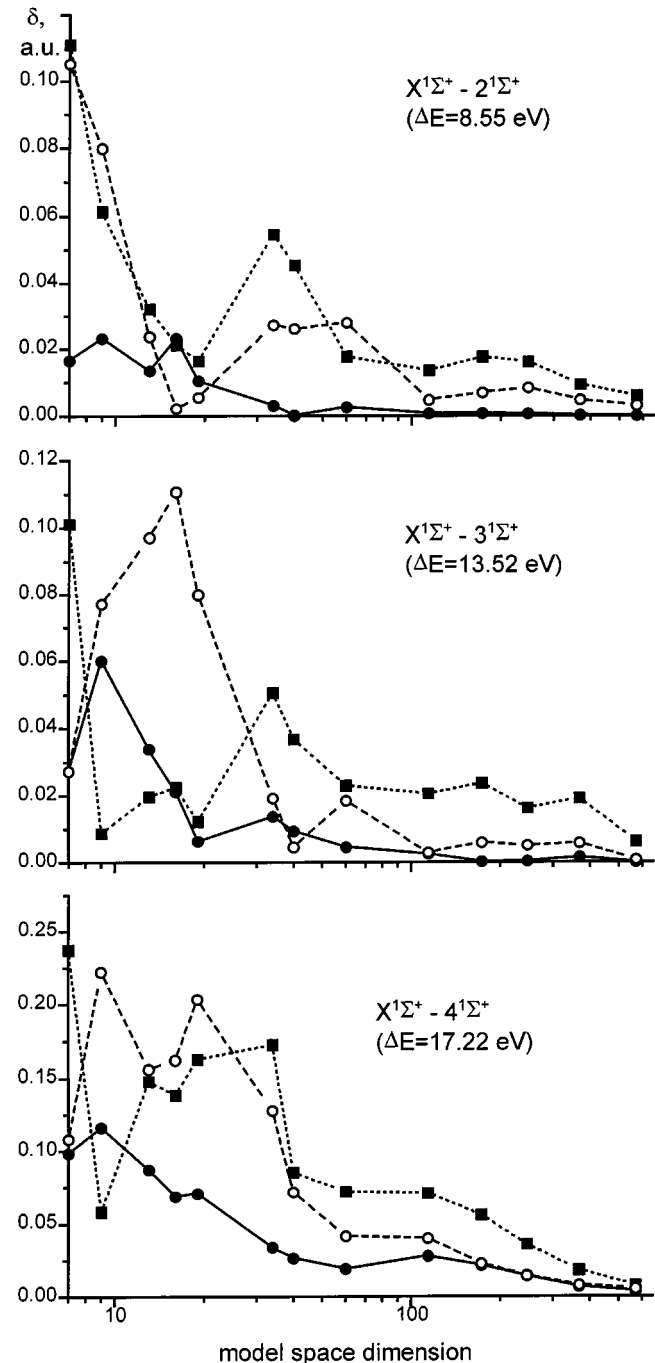

Fig. 1. Absolute deviations (δ) of calculated transition dipole moments in CH^+ from the corresponding full CI values [24]. Solid squares: model space CI results, empty circles: $\mathbf{D}_{if}^{DL}$, solid circles: $\mathbf{D}_{if}^{FF}$.

eigenvectors do not comprise any outer space component, the finite-field TDM values implicitly incorporate the bulk of direct outer-space contributions which can be necessary for obtaining quantitative results. The latter statement is valid both for conventional (state-universal) and intermediate (state-specific) effective Hamiltonians with various choices of wave-operator normalization conditions.

The accuracy of FF TDM estimates should decrease with the increase of transition energies.

Our analysis concerns the case of fixed (field-independent) model spaces. However, our FF scheme can be immediately combined with the field-dependent optimization of the model space (*e.g.* by a state-average MC-SCF procedure), thus enabling one to take advantage from the proper account for orbital relaxation effects.

The $\mathbf{D}_{if}^{FF}$ values are uniquely defined by the field-dependent effective Hamiltonian, and the construction of the effective dipole operator is avoided. This seems to be of particular importance for state-selective (intermediate Hamiltonian) theories [8] and model approaches suffering from the difficulties in consistent definition of different effective operators. Finally, the present analysis can give some insight into the theoretical background and limitations of TDM calculations within field-dependent model Hamiltonian approaches such as the polarization pseudopotential method [29–31].

References

1. H.D. Cohen, C.C.J. Roothaan, J. Chem. Phys. **43**, S34 (1965).
2. J.A. Pople, J.W. McIver, N.S. Ostlund, J. Chem. Phys. **49**, 2965 (1968).
3. A.J. Sadlej, J. Chem. Phys. **75**, 320 (1981).
4. G.H.F. Diercksen, A.J. Sadlej, J. Chem. Phys. **75**, 1253 (1981).
5. P.M. Kozlowski, E.R. Davidson, Int. J. Quantum Chem. **53**, 149 (1995).
6. M. Tamanis, M. Auzinsh, I. Klincare, O. Nikolayeva, R. Ferber, A. Zaitsevskii, E.A. Pazyuk, A.V. Stolyarov, J. Chem. Phys. (in press).
7. S. Adamson, A. Zaitsevskii, N.F. Stepanov, J. Phys. B: At. Mol. Opt. Phys. (submitted).
8. Ph. Durand, J.P. Malrieu, Adv. Chem. Phys. **67**, 321 (1987).
9. U. Kaldor, Lect. Notes Chem. **52**, 199 (1989).
10. I. Lindgren, J. Phys. B: At. Mol. Phys. **7**, 2441 (1974).
11. V. Hurtubise, K.F. Freed, Adv. Chem. Phys. **83**, 465 (1993).
12. V. Hurtubise, K.F. Freed, J. Chem. Phys. **99**, 7946 (1993).
13. P.J. Ellis, E. Osnes, Rev. Mod. Phys. **49**, 777 (1977).
14. H. Sun, K.F. Freed, J. Chem. Phys. **88**, 2659 (1988).
15. V. Kvasnicka, Int. J. Quantum Chem. **24**, 335 (1983).
16. V. Hurtubise, J. Chem. Phys. **100**, 4955 (1994).
17. L.T. Redmon, Phys. Rev. A Gen. Phys. **25**, 2453 (1982).
18. F. Jorgensen, Mol. Phys. **29**, 1137 (1975).
19. J.P. Malrieu, Ph. Durand, J.P. Daudey, J. Phys. A: Math. Gen. **18**, 809 (1985).
20. A. Zaitsevskii, J.P. Malrieu, Int. J. Quantum Chem. **55**, 117 (1995).
21. A. Zaitsevskii, J.P. Malrieu, Theor. Chem. Acc. **96**, 269 (1997).
22. J.P. Malrieu, in *Recent Progress in Many-Body Theories*, Vol. 4, edited by E. Schachinger, H. Mitter, H. Sormann (Plenum Press, New–York-London, 1995), p. 109.
23. A.J. Sadlej, Coll. Czech. Chem. Commun. **53**, 1995 (1988).
24. J. Olsen, A.M. Sanchez de Meras, H.J.A. Jensen, P. Jorgensen, Chem. Phys. Lett. **154**, 380 (1989).
25. A. Zaitsevskii, R. Cimiraglia (unpublished).
26. K. Freed, Lect. Notes Chem. **52**, 1 (1989).
27. J. Miralles, O. Castell, R. Caballol, J.P. Malrieu, Chem. Phys. **172**, 33 (1993).
28. C. Petrongolo, R.J. Buenker, S.D. Peyerimhoff, J. Chem. Phys. **76**, 3655 (1982).
29. S. Hameed, J. Phys. B: At. Mol. Phys. **6**, 2055 (1973).
30. P. Fuentealba, H. Preuss, H. Stoll, L. von Szentpaly, Chem. Phys. Lett. **89**, 418 (1982).
31. W. Mueller, J. Flesh, W. Meyer, J. Chem. Phys. **80**, 3297 (1984).