Theor Chem Acc (2000) 105:169–172
DOI 10.1007/s002140000202

Theoretical
Chemistry Accounts

*Regular article*

# Inexpensive and accurate predictions of optical excitations in transition-metal complexes: the TDDFT/PBE0 route

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Received: 8 August 2000 / Accepted: 7 September 2000 /

**Abstract.** Time-dependent density functional theory (TDDFT) is applied to calculate vertical excitation energies of three representative transition metal complexes. The computational model (PBE0) is obtained by combining the Perdew-Burke-Erzenrhof (PBE) generalized gradient functional with a predetermined amount of exact exchange. Our results show that the TDDFT/PBE0 model represents a cheap and reliable tool for the computation of optical excitations for transition metal complexes.

**Key words:** Time-dependent density functional theory – Perdew-Burke-Erzenrhof model – Transition metal hexafluoride complexes

A quantitative understanding of molecular electronic excited states is important in many domains, including spectroscopy, photochemistry, and the design of optical materials. The prediction or interpretation of the discrete part of the electronic spectrum is a demanding task for theoretical methods, especially when medium- and large-size molecules of chemical interest are involved. Thus, an inexpensive yet accurate method to calculate vertical excitation energies would be very useful. This is particularly true in the field of transition metal chemistry, where the size of the systems and the number of electrons prevent the application of the most refined computational tools used in the study of excited electronic states of organic species. As a matter of fact, only semiempirical methods are routinely applicable, but their range of validity is not easily defined and different chemical applications often require different parameterizations.

Density functional theory (DFT) has been remarkably successful at providing a means to evaluate a variety of ground state properties with an accuracy close to that of post-Hartree-Fock (HF) methods [1]. Since DFT methods rectify many problems of the HF approximation at comparable computational cost, there is currently a great interest in extending the DFT approach to excited electronic states. In this context, the time-dependent (TD) generalization of the DFT theory (TDDFT) offers a rigorous route to the calculation of the dynamic response of the charge density [2]. Combining this with linear response theory allows the calculation of vertical electronic excitation spectra [3].

Several tests [4–6] have shown that current functionals, including hybrid HF/DFT models, provide results for low excitation energies usually superior to the those obtained by time-dependent HF methods (TDHF), or by the configuration interaction with singles excitations (CIS) approach. In particular, we have recently introduced the so-called PBE0 model (a hybrid HF/DFT approach based on the Perdew-Burke-Erzenrhof (PBE) exchange-correlation functional [7]), which overcomes many of the problems encountered with standard functionals, providing accurate excitation energies to both valence and Rydberg states [8, 9]. The strength of the PBE0 model is that the parent PBE functional does not contain any parameter fitted to experimental data and that a predefined amount of HF exchange is added self-consistently to the DFT contribution. In other words, the PBE0 can be considered a true non-empirical DFT approach, which provides, at the same time, accurate numerical results for a number of ground and excited state properties [8–12]. Here we will show that accurate reproductions of electronic spectra are also possible using the PBE0 model for molecules containing heavy transition metals. To the best of our knowledge this is the first time that TDDFT and PBE0 have been applied to this goal.

As a difficult playground, we have chosen the hexafluorides of chromium, molybdenum, and tungsten ($CrF_6$, $MoF_6$, and $WF_6$), which show electronic spectra typical of transition metal complexes, dominated by charge-transfer bands. Some quantum mechanical computations are available for excited states of $MoF_6$

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and $WF_6$ [13–15], together with detailed experimental data [16, 17], whereas the existence of $CrF_6$ is still a matter of discussion [18, 19]. In this last case, theoretical predictions of the optical spectrum could give some hints to experimentalists for the identification of such a species.

All the computations presented in this communication have been carried out using the development version of the Gaussian program [20], in which the PBE0 model has been recently implemented [10, 21]. For all the ground and excited state computations, the molecules have been frozen in $O_h$ symmetry, which corresponds to the most stable isomer for all the molecules [14, 22, 23]. Furthermore, we have considered only singlet excited states.

On the basis of previous experience [8, 24], we have chosen the quasi-relativistic effective core potentials of Stevens and co-workers [25] (hereafter referred to as SBK) for the metals and the 6-311 + G(d,p) basis set for the fluorine atoms [26]. The standard SBK basis set has been augmented with two sets of f functions [27] for geometry optimizations, whereas it has been left unmodified in the computation of excitation energies. As a matter of fact, several test computations have shown that f functions are needed to obtain converged geometries, whereas excitation energies are converged to better than 0.2 eV using the original valence basis set.

The calculations have been carried out using either the experimental structural parameters (available only for $MoF_6$ and $WF_6$ [28, 29]) or the optimized PBE0 geometries. The bond lengths collected in Table 1 confirm the accuracy of the PBE0 model in the prediction of molecular structures.

According to a simple angular overlap model, the $MF_6$ species can be described as $d^0$ complexes, with a formal charge of +6 on Cr, Mo, and W. Our computations indicate that all valence occupied molecular orbitals (MOs) have mainly ligand character and that the virtual orbitals are dominated by contribution from the metal d orbitals. However, the M-F bond has a large covalent character owing to the back-donation from ligand to metal. In fact a natural population analysis (NPA) [30] leads to charges of +1.62, +2.38, and +2.47 for Cr, Mo, and W, respectively.

**Table 1.** Comparison between PBE0 and experimental bond lengths (Å) for octahedral $MF_6$ complexes (M = Cr, Mo, W)

| Molecule | PBE0 | Exp.[a] |
|---|---|---|
| $CrF_6$ | 1.718 | – |
| $MoF_6$ | 1.836 | 1.820(3) |
| $WF_6$ | 1.839 | 1.832(3) |

[a] From refs. [28] and [29]

In Table 2 are reported the calculated vertical transitions for $MoF_6$, together with the available experimental and post-HF results [15, 16]. All the excited states are dominated by single excitations from valence MOs (having ligand non-bonding or metal-ligand bonding characters) to the $t_{2g}$ orbitals with large d characters for the central metal atom. Thus these valence electronic transitions can be described as charge-transfer excitations from ligand to metal. The very high first ionization potential of the complex (15.2 eV) precludes the existence of Rydberg transitions in the considered spectral range. There is an overall good agreement between PBE0 and experimental values, the largest difference being 0.4 eV. Furthermore, our results are close to those provided by the much more expensive symmetry-adapted-cluster configuration interaction (SAC-CI) method [15]. It must be noted, anyway, that this last approach does not predict the highest energy transitions at about 10.0 eV [15].

Our assignment follows the experimental indications for two out of six transitions, which are classified as excitations from an $e_g$ orbital ($\sigma$ orbitals of the ligands) to a $t_{2g}$ orbital of the metal (d orbital). The other bands are dominated by excitations from $\pi$ orbitals of the fluorine atoms (belonging to the $t_{1u}$ and $t_{2u}$ representation) and are assigned in agreement with SAC-CI calculations [15]. The highest band at 10.0 eV arises from an excitation of a $\pi$ orbital of the ligand belonging to the $t_{1g}$ representation. These transitions are not significantly affected by variations of the geometrical parameters (see Table 2), the calculated values being very close to the experimental data.

Similar behavior has been found for the transitions of $WF_6$ (see Table 3). Also in this case there is a good overall agreement between PBE0 and experimental values and even better results are obtained using the PBE0 bond length. The two transitions centered at 7.4 and 8.5 eV are assigned in agreement with experimental indications [16]. The lowest and the highest transitions correspond to excitations from ligand MOs with $t_{1u}$ and $t_{1g}$ symmetry, respectively, whereas the other two transitions are generated from $t_{2g}$ and $e_g$ orbitals. A different

**Table 2.** Vertical excitation energies (eV) for $MoF_6$. All values have been computed using the experimental geometry, unless otherwise noted

| SAC-CI[a] | | PBE0 | | | Exp.[b] | |
|---|---|---|---|---|---|---|
| Main transition | $\Delta\nu$ | Main transition | $\Delta\nu$ | $\Delta\nu^c$ | Main transition | $\Delta\nu$ |
| $t_{1u} \rightarrow t_{2g}$ | 5.55 | $t_{1u} \rightarrow t_{2g}$ | 5.98 | 5.88 | $t_{1g} \rightarrow t_{2g}$ | 5.90 |
| $t_{2u} \rightarrow t_{2g}$ | 6.61 | $t_{2u} \rightarrow t_{2g}$ | 6.18 | 6.35 | $t_{1u} \rightarrow t_{2g}$ | 6.54 |
| $t_{1u} \rightarrow t_{2g}$ | 7.26 | $t_{1u} \rightarrow t_{2g}$ | 7.38 | 7.35 | $t_{2u} \rightarrow t_{2g}$ | 7.12 |
| $t_{2g} \rightarrow t_{2g}$ | 8.91 | $e_g \rightarrow t_{2g}$ | 8.77 | 8.64 | $e_g \rightarrow t_{2g}$ | 8.62 |
| $e_g \rightarrow t_{2g}$ | 9.49 | $e_g \rightarrow t_{2g}$ | 9.15 | 9.17 | $e_g \rightarrow t_{2g}$ | 9.22 |
| – | – | $t_{1g} \rightarrow t_{2g}$ | 10.00 | 10.03 | $t_{1u} \rightarrow t_{2g}$ | 10.04 |

[a] Ref. [15]
[b] Ref. [16]
[c] Calculated using the PBE0 geometry of Table 1

**Table 3.** Vertical excitation energies (eV) for $WF_6$ and $CrF_6$

| $WF_6$ | | | | | $CrF_6$ | |
|---|---|---|---|---|---|---|
| PBE0 | | | Exp.[a] | | PBE0 | |
| Main transition | $\Delta\nu^b$ | $\Delta\nu^c$ | Main transition | $\Delta\nu$ | Main transition | $\Delta\nu^c$ |
| $t_{1u} \rightarrow t_{2g}$ | 7.13 | 6.97 | $t_{1g} \rightarrow t_{2g}$ | 7.23 | $t_{1u} \rightarrow t_{2g}$ | 3.76 |
| $t_{2u} \rightarrow t_{2g}$ | 7.36 | 7.85 | $t_{2u} \rightarrow t_{2g}$ | 8.05 | $t_{2u} \rightarrow t_{2g}$ | 4.32 |
| $t_{1u} \rightarrow t_{2g}$ | 8.47 | 8.50 | $t_{1u} \rightarrow t_{2g}$ | 8.60 | $t_{1u} \rightarrow t_{2g}$ | 5.84 |
| $t_{2g} \rightarrow t_{2g}$ | 8.94 | 8.82 | $t_{1u} \rightarrow t_{2g}$ | 8.94 | $e_g \rightarrow t_{2g}$ | 7.11 |
| $e_g \rightarrow t_{2g}$ | 9.62 | 9.62 | $a_g \rightarrow t_{2g}$ | 10.03 | $t_{1g} \rightarrow t_{2g}$ | 8.51 |
| $t_{1g} \rightarrow t_{2g}$ | 11.43 | 11.01 | $e_g \rightarrow t_{2g}$ | 11.05 | – | – |

[a] Ref. [16]
[b] Computed using the experimental geometry
[c] Computed using the PBE0 geometry of Table 1

assignment has been proposed in the experimental study [16], but, as before, our assignment supports older Xα computations [14].

Table 3 contains also the optical transitions for $CrF_6$, together with our assignment. As mentioned above, the existence of this molecule is still a matter of discussion, so that excitation spectra are not yet available. As expected, there is a correlation between the excitation energies computed for $CrF_6$ and those of the other two complexes. This correlation is well evidenced in Fig. 1. The most remarkable feature of this plot is the parallel trend observed along the series, which strongly supports, in our opinion, the PBE0 assignment for the transitions in $CrF_6$.

On the basis of the results for the other members of the series, we estimate that these bands are accurate to about 0.2–0.3 eV, with a somewhat larger error for the $2t_{2u} \rightarrow t_{2g}$ transition. As a final remark, we note that none of the calculated transitions for $CrF_6$ can be detected in the UV spectrum of $CrF_5$ [18], thus ruling out the disproportionation mechanism of this species into $CrF_4$ and $CrF_6$.

In summary, the results obtained for $MF_6$ complexes (M = Cr, Mo, W) are in fairly good agreement with the available experimental data and their accuracy is close to that delivered by the most refined and time-consuming post-HF methods. Taking into account also the reasonable computer requirements of the PBE0 model and its documented accuracy for several other physicochemical properties along the whole Periodic Table, we think that new exciting perspectives are open for the study of photochemical processes involving metal atoms and biologically interesting molecules.

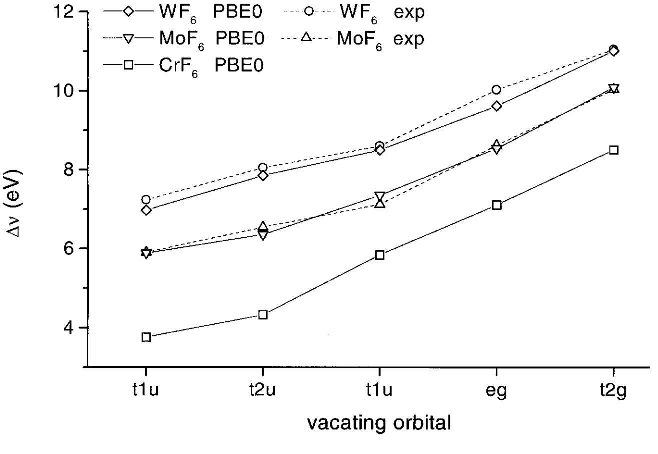

**Fig. 1.** Comparison between experimental and TDDFT/PBE0 vertical excitation energies of the $MF_6$ complexes. The theoretical values have been computed using the geometrical parameters of Table 1

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