



ELSEVIER

Journal of Electron Spectroscopy and Related Phenomena 123 (2002) 345–363

---

---

**JOURNAL OF  
ELECTRON SPECTROSCOPY**  
and Related Phenomena

---

---

www.elsevier.com/locate/elspec

# Kohn–Sham orbitals and orbital energies: fictitious constructs but good approximations all the same

Sebastien Hamel<sup>a,b,\*</sup>, Patrick Duffy<sup>c</sup>, Mark E. Casida<sup>d</sup>, Dennis R. Salahub<sup>b,e,f</sup><sup>a</sup>*Departement de Physique, Universite de Montreal, Case Postale 6128, Succursale Centre-ville, Montreal, Quebec H3C 3J7, Canada*<sup>b</sup>*Centre de Recherche en Calcul Applique (CERCA), 5160 Boulevard Decarie, Bureau 400, Montreal, Quebec H3X 2H9, Canada*<sup>c</sup>*Kwantlen University College, Richmond Campus, 8771 Lansdowne Road, Richmond, BC V6X 3V8, Canada*<sup>d</sup>*Laboratoire d'Etudes Dynamiques et Structurales de la Selectivite (LEDSS) Universite Joseph Fourier, 38041 Grenoble, France*<sup>e</sup>*Departement de Chimie, Universite de Montreal, Case Postale 6128, Succursale Centre-ville, Montreal, Quebec H3C 3J7, Canada*<sup>f</sup>*The Steacie Institute for Molecular Sciences, National Research Council of Canada, 1000 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada*

---

## Abstract

Kohn and Sham introduced orbitals into density–functional theory (DFT) as a set of physically meaningless auxiliary quantities useful only for calculating the total energy and charge density. While the traditional view is that Kohn–Sham orbitals do not approximate anything, Duffy et al. [*Phys. Rev. A* 50 (1994) 4707] showed that Kohn–Sham orbitals calculated using approximate exchange–correlation (xc) potentials could provide excellent approximations to spherically averaged momentum distributions, despite the fact that the corresponding Kohn–Sham orbital energies do not provide good approximations to ionization potentials when typical common present-day functionals are used. Since the original conclusions were based upon approximate xc potentials, the question arises as to how these conclusions might change when the same orbitals and orbital energies are calculated using an exact (or nearly exact) xc potential. For example, it has long been known that the highest occupied molecular orbital energy should give the *exact* ionization potential when the DFT xc functional is exact, but that this is not observed for approximate potentials. What about the other orbital energies? Long regarded as artifactual, we show that (1) Kohn–Sham orbital energies calculated using the exact Kohn–Sham exchange potential are actually better approximations to experimental ionization potentials than are Hartree–Fock orbital energies calculated via Koopmans' theorem. We also show that (2) there are only negligible differences between spherically averaged momentum distributions calculated from HF orbitals and from Kohn–Sham orbitals calculated using the exact Kohn–Sham exchange potential, thus partially addressing the question of how the use of the exact Kohn–Sham potential will affect predictions for electron momentum spectroscopy. In addition to the two numbered observations above can be added that (3) it is quite remarkable that a nominally initial state theory such as DFT can do so well in describing ionization, a phenomenon which one expects to be sensitive to both initial and final states (before and after the ionization event). © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Kohn–Sham orbitals; Orbital energies; Momentum distributions; Exact exchange functional; Optimized effective potential

---

---

\*Corresponding author. Departement de Chimie, Universite de Montreal, Case Postale 6128, Succursale Centre-ville, Montreal, Quebec H3C 3J7, Canada. Tel.: +1-514-3436-1111; fax: +1-514-3432-468.  
E-mail address: hamels@magellan.umontreal.ca (S. Hamel).

## 1. Introduction

Due to its efficiency, density functional theory (DFT) has become a method of choice in computa-

tional chemistry. DFT allows us to handle large molecules with medium sized basis sets and small molecules with large basis sets. This latter fact has motivated the electron momentum spectroscopy (EMS) community to investigate the value of DFT orbitals for analyzing experimental results [1–14].

While the results have been in general very encouraging, at least two troubling problems have remained unresolved. The first of these is that all DFT calculations to date carried out for comparison with EMS results have been based on *approximate* exchange-correlation (xc) functionals which are known to fall off too rapidly at large  $r$ , which could conceivably lead to exaggerations in the small  $p$  part of theoretical spherically averaged momentum distributions (MDs). The second problem is that, although DFT orbitals seem to be a good descriptor of ionization cross sections, the orbital energies (calculated using the same approximate functionals) grossly underestimate the corresponding principal ionization potentials. This leads to the question of how DFT can be successfully applied to EMS when the orbitals and their energies seem to provide no more than a partial description of the ionization process. In this article, we report calculations of DFT MDs and orbital energies with the exact (or nearly so) Kohn–Sham exchange potential. In so doing, we show that the two above mentioned problems may be at least partially resolved by the use of a more exact xc potential.

Electron momentum spectroscopy has emerged, since the first experiments in the late 1960s and early 1970s, as a unique tool for the study of the electronic structure of atoms and molecules [10,15–17]. EMS is a technique similar to photoelectron spectroscopy where electrons, instead of photons, ionize the target atom or molecule. In common with photoelectron spectroscopy, it can obtain the binding energy spectra of atoms and molecules in both valence and core regions. EMS, however, does this without having to rely on exotic photon optics or synchrotrons to generate photons of sufficient energy to measure binding energy spectra past 25 eV. The main strength of EMS, however, lies in its additional ability to obtain binding energy spectra differential with respect to electron momentum. These experimental momentum profiles (XMPs), which run from near zero up to  $\sim 3$  atomic units of momentum, can be

compared with theoretical MDs as a test of the accuracy of the approximations made in the calculations (see, for example, Ref. [10]). Also, since the MDs probe primarily the low-momentum region, this technique is very useful as a test of the theoretical description of the large  $r$  region.

As EMS studies have progressed to larger molecules (for example, acetone [7]) however, a limitation has been encountered in the theoretical calculations to which the experiment is to be compared. Specifically, the computational power necessary to calculate the MDs using configuration interaction (CI) and Roothaan Hartree–Fock calculations (traditionally included in the studies) limits the accuracy of the calculation which may be included. If calculations of high accuracy are to be included in future studies of larger molecules, it is therefore of interest to investigate new, less computationally demanding methods for their calculation. One such computational method which has shown much promise and a great deal of success is density functional theory.

Preliminary work investigating the use of Kohn–Sham orbitals for the calculation of MDs was carried out by Duffy et al. [13]; a study of acetone by Zheng et al. [7] also demonstrated the potential of DFT to EMS. A more comprehensive application of DFT to the calculation of MDs, carried out by Duffy [18], showed universal success for the row 2 and 3 hydrides tested. Studies by Brion and co-workers [1–6] have likewise shown the potential of DFT for calculation of MDs.

In spite of the many studies relating the MDs calculated by density functional theory to the EMS experimental momentum profile, and the general success of the applications, at least one problem remains to cast a shadow of doubt over the contention that DFT provides a good approximation for describing EMS. This problem is that all DFT calculations used in the EMS studies to date used approximate expressions for the exchange-correlation potential. This leaves doubt about how well DFT should work for EMS in the limit where the exact functional (and hence the exact Kohn–Sham orbital) is used. Thus, while the MDs generated from these calculations fit the data well, it was difficult to draw any definitive conclusions about DFT itself and the quality of the MDs it should generate for comparison with EMS experimental results.

With the introduction of the optimized effective potential (OEP) to DFT, however, the concern just raised may be addressed, as the OEP has been shown to be (up to a certain linear response approximation [19]) the exact DFT exchange potential. This, coupled with the linking of DFT to the Green Function method [13], means that MDs generated using this new, exact, exchange potential should match those from CI and Green Function calculations very closely in cases where correlation is not a significant factor in their calculation. It is one of the central purposes of this paper to test this assumption, and in the process to determine if Kohn–Sham orbitals do indeed have any basis in physical reality.

In Section 2 we briefly outline the principles of exchange-only OEP and the use of Kohn–Sham density functional theory as an approximation to Dyson’s equation. In Section 4 OEP results for the ionization potentials of 26 molecules and the momentum distributions of orbitals of  $C_2H_2$ , CO, HF,  $H_2O$ ,  $NH_3$  and  $CH_4$  are presented after a brief discussion of the finite basis set convergence for the exchange-correlation potential, the orbital energies and the momentum distributions.

## 2. Theoretical background

Much of the motivation for using DFT orbitals and orbital energies to describe ionization phenomena comes from the close analogies between Dyson’s quasiparticle equation and the Kohn–Sham equation of DFT. In this section, we first review this analogy and then discuss how the exact exchange-only Kohn–Sham orbitals can be calculated.

A well-established theoretical method for describing ionization events is via Dyson’s quasiparticle equation

$$[\hat{h}_H + \hat{\Sigma}_{xc}(\omega_1)]\phi_1(\mathbf{r}) = \omega_1\phi_1(\mathbf{r}) \quad (2.1)$$

a one-electron Schrödinger-like equation. Here:

$$\hat{h}_H = -\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (2.2)$$

and the exchange-correlation operator  $\hat{\Sigma}_{xc}$  includes many-body effects such as correlation, relaxation, dynamic polarization and a correction to the self-

interaction error in the Coulomb part of the Hartree hamiltonian. The Dyson orbital energies in Eq. (2.1) are minus the ionization potentials and electron affinities. The Dyson orbitals corresponding to the ionization potential solutions are ion-neutral overlaps:

$$\begin{aligned} \phi_1(\mathbf{r}_1\sigma_1) &= \phi(1) \\ &= \sqrt{N} \int \dots \int \Phi_1^{N-1*}(2, 3, \dots, N) \\ &\times \Phi_1^N(1, 2, 3, \dots, N) d2d3 \dots dN, \end{aligned} \quad (2.3)$$

and are closely related to ionization cross-sections. The densities of these orbitals sums to the total charge density:

$$\rho(\mathbf{r}) = \sum_i^{\text{ionization}} |\phi_i(\mathbf{r})|^2 \quad (2.4)$$

In the exchange-only approximation, i.e., when  $\hat{\Sigma}_{xc}(\omega_1) = \hat{\Sigma}_x^{\text{HF}}$ , the quasiparticle equation becomes the Hartree–Fock equation.

A superficially similar one-electron-like Schrödinger equation is the Kohn–Sham equation:

$$\left[ -\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (2.5)$$

where:

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) \quad (2.6)$$

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \quad (2.7)$$

The exchange-correlation (xc) potential is exact when the sum of the densities of the lowest  $N$  occupied Kohn–Sham orbitals is the exact charge density:

$$\rho(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2 \quad (2.8)$$

While there is an obvious resemblance between the Kohn–Sham (KS) and Dyson equations, there are also important differences, as pointed out by Kohn and Sham themselves and also Casida [20,21]. First and foremost, the KS equation is the orbital equation for a fictitious system of non-interacting particles moving in a local potential while the Dyson equation refers to quasi-particles moving in a po-

tential with an orbital-energy dependent contribution. Secondly, there are  $N$  orthonormal KS orbitals while the Dyson orbitals are neither orthogonal, nor normal, nor finite in number.

But this does not prevent the Kohn–Sham orbitals from being good candidates for approximating individual Dyson orbitals in the sense of the “target Kohn–Sham approximation”—that is, for each ionization  $I$ :

$$\phi_1^{\text{Dyson}}(\mathbf{r}) = S_1 \psi_i^{\text{KS}}(\mathbf{r}) \quad (2.9)$$

for some DFT orbital  $\psi_i^{\text{KS}}$ . The spectroscopic factor,  $S_1$ , is typically close to one for outer valence ionization.

In practice, the Kohn–Sham orbitals were found to be very similar to Dyson orbitals for valence ionization (see Ref. [13] and references therein). It is difficult to infer exactly from these studies just how well Kohn–Sham orbitals actually do approximate Dyson orbitals. For one thing, Dyson orbitals tend to resemble Hartree–Fock orbitals just as much as Kohn–Sham orbitals, so it is hard to judge in the correlated case whether Kohn–Sham orbitals are approximating Hartree–Fock orbitals better or whether they are in fact approximating the fully correlated Dyson orbitals (see however Koren et al. [22].) Another problem is that the use of approximate exchange–correlation potentials might be expected to lead to systematic errors in DFT orbitals and their MDs. In particular, it is known that that LDA and GGA functionals tend to fall off too rapidly. The physical effect of an such an xc potential is that an electron in the large- $r$  region experiences the full non-self-interaction-corrected Hartree potential for  $N$  electrons instead of the correct potential for  $(N-1)$  electrons. This makes the electron less bound than it should be, its position space orbital too diffuse, and the corresponding MDs probably have too large an amplitude at small momentum. Finally, a third problem is that, while DFT orbitals calculated using approximate functions seem to describe ionization cross-sections reasonably well, the corresponding orbital energies drastically underestimate ionization potentials. This, of course, is related to underbinding due to the too rapid fall off of approximate xc potentials at large distance.

It is now possible to perform much better tests of how well exact (or nearly exact) DFT orbitals and orbital energies can describe the ionization event. The key quantity required for this calculation is the exact exchange–correlation potential. Nearly exact xc potentials can be constructed beginning from high quality ab initio charge densities. So far this has been done for only a few systems [23–25]. Alternatively we can restrict ourselves to an exchange-only theory and seek the DFT potential which is exact in the sense that it produces the Hartree–Fock charge density. This is essentially the problem solved in the OEP method used here. That is, the potential which comes out of the OEP method is for all intents and purposes the same as the exact exchange-only DFT potential.

The OEP is a form of constrained HF which gives results almost equivalent to HF. Even if correlation may turn out to have unexpected consequences for DFT description of EMS, for the moment our understanding is that there is a serious error in the long range behavior of the approximate xc potentials which is dominated by the exchange part of the potential.

The exchange-only OEP equation was first given by Sharp and Horton in 1953 [26] as an elegant solution to Slater’s problem [27] of trying to find the optimal local potential which most closely approximates the kernel of the HF exchange operator:

$$\Sigma_x^\sigma(\mathbf{r}, \mathbf{r}') \sim \delta(\mathbf{r} - \mathbf{r}') v_x^\sigma(\mathbf{r}) \quad (2.10)$$

Of course, the nonlocal operator  $\Sigma_x^\sigma$  can never be fit exactly by a simple multiplicative function  $v_x^\sigma$ , so we have introduced [28] the symbol “ $\sim$ ” to indicate that something remains to be done to make the above idea precise. This “something” consists of finding the  $v_x^\sigma$  whose orbitals minimize the Hartree–Fock energy expression. This turns out to be equivalent to performing a least-square fit using as weight function the generalized susceptibility of linear response theory [28]. The generalized susceptibility describes the linear response of the one-electron density matrix to an arbitrary perturbation. Numerical calculations were not carried out until more than 20 years after Sharp and Horton, when Talman and Shadwick applied the method to calculate  $v_x$  for atoms [29].

More recently Krieger et al. [30] have generalized the calculations of Talman and co-workers to include spin. We are not going to derive the OEP equation again since this has already been done many times before in the literature [20,28,31–34,G99,IHB99]. Instead we are going to use the OEP method to investigate how well exact exchange-only DFT orbitals and orbital energies describe the ionization event.

### 3. Computational details

Resolution-of-the-identity OEP (RI-OEP) and HF (RIHF) calculations were carried out using version 3.1 of DEMON-DYNARHO [DEMON for “densité de Montréal” and DYNARHO for “dynamic response of the charge density (rho)”] [37] with a local density approximation (LDA) initial guess carried out by another program in the DEMON suite of programs, namely version 4.0 of DEMON-KS [38]. The spherically averaged orbital momentum distributions were calculated from the orbitals with the HEMS program [39].

For the ionization potentials, to follow up on previously published work [28,40], the orbital basis set was taken from Sadlej [41]. This is a medium-sized basis set, sufficient for valence-type orbitals. In all cases, we used all six gaussian cartesian *d*-functions. For the momentum distributions, in order to compare with previously published results, Dunning’s aug-cc-pv5z [D89,KDH92] basis set was used in the OEP calculations.

Both DYNARHO and KS use auxiliary functions to eliminate costly four-center integrals as described in more detail elsewhere [28,40]. In addition, the KS calculation requires use of a grid. The unpruned EXTRAFINE angular grid (194 angular points) and 32 radial points (for a total of 6208 grid points per atom) were used.

Convergence criteria for the KS self-consistent field (SCF) calculations were set at  $10^{-8}$  hartree on the total energy and  $10^{-8}$  atomic units on the charge density auxiliary function fitting coefficients. Convergence criteria for the OEP SCF calculations in DYNARHO were set to  $10^{-8}$  hartree on the total energy for eight consecutive iterations, except for

molecules where convergence proved more difficult. For these molecules the convergence criteria were loosened to  $10^{-7}$  hartree (cyclopropene, diazine,  $\text{HN}_3$ , NNO and  $\text{C}_2\text{H}_2$ ) and  $10^{-6}$  hartree (allene and  $\text{CH}_3\text{CCH}$ ).

Experimental geometries taken from Ref. [44] and Ref. [45] were used.

## 4. Results

### 4.1. Convergence with respect to basis set

#### 4.1.1. Potential shift

As with any mathematical potential function, the OEP potential is defined up to a constant usually fixed by some physical property. Here this constant is fixed by a very important property of the exchange-only OEP potential: the exchange-only OEP is such that the energy of the OEP highest occupied molecular orbital (HOMO) is the same as the energy of the Hartree–Fock HOMO calculated with the same orbitals (the OEP orbitals) which is equivalent, for the exact potential, to having the exchange-correlation potential go asymptotically to zero [KLI90]. So, in principle, enforcing either one of these two conditions fixes the arbitrary constant. However, in practice, with finite-basis computations, it is typically impossible to satisfy simultaneously the asymptotic condition and the HOMO energy condition, so a choice has to be made.

Although it is trivial to force  $v_x^\sigma$  to go asymptotically to zero by constructing it as an expansion of auxiliary functions all of which go asymptotically to zero (as is done here), this in no way guarantees the correct *long-range* behavior of  $v_x^\sigma$  which is what we would really like to have. In particular, a potential which goes too quickly to zero will underbind  $-\epsilon_{\text{HOMO}}^\sigma$ , while a potential which goes too slowly to zero will overbind  $-\epsilon_{\text{HOMO}}^\sigma$ .

On the other hand, accurate Kohn–Sham orbital energies are an important objective of our OEP work for later use in time-dependent density-functional theory calculations. Of these orbital energies, that of the HOMO is particularly critical since this fixes the asymptotic behavior of the exchange-correlation potential.

We have chosen to enforce the HOMO energy condition. We do this by shifting the potential by:

$$\Delta^\sigma = \left\langle \psi_{\text{HOMO}}^\sigma | \hat{\Sigma}_x^\sigma - v_x^\sigma | \psi_{\text{HOMO}}^\sigma \right\rangle \quad (4.1)$$

on every SCF iteration.

The size of the shift is symptomatic of errors that affect the very large  $r$  region and will be important primarily for virtual orbitals. Its effect is not apparent for the occupied levels, at least for the molecules studied. For example, the MDs of  $\text{CH}_4$  (Fig. 1) for the aug-cc-pv5z and cc-pv5z basis sets are identical

while the potentials were shifted by  $-22.01$  and  $-459.71$  eV, respectively. An example of large positive shifts may be found with the HF molecule for the aug-cc-pv5z and cc-pv5z basis sets with 50.62 and 194.5 eV shifts, respectively.

Nevertheless we prefer to seek the basis set giving the lowest energy while giving also a small shift. The shifts can be found in Table 1 for seven small molecules and for the sadlej, sadlej+ (sadlej with added diffuse functions), cc-pv5z and aug-cc-pv5z basis sets.

In view of the results, it is difficult to single out

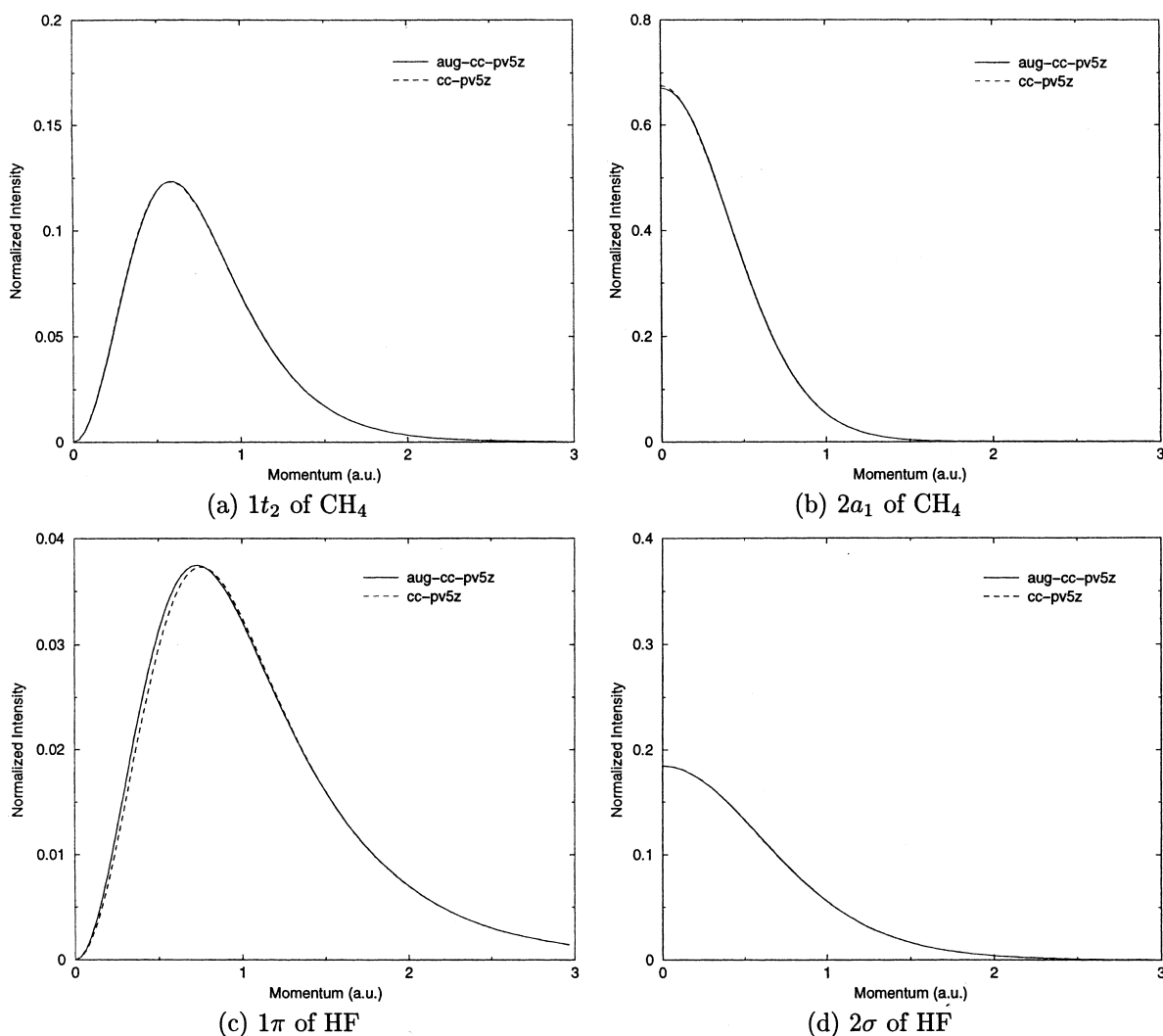


Fig. 1. OEP results with cc-pv5z and aug-cc-pv5z orbital basis sets.

Table 1

Shift (eV) in the exchange-correlation potential for various basis sets and 7 small molecules

Basis	C <sub>2</sub> H <sub>2</sub>	CO	CH <sub>4</sub>	H <sub>2</sub> O	NH <sub>3</sub>	HF	C <sub>2</sub> H <sub>4</sub>	MAS <sup>a</sup>
aug-cc-pv5z	−4.51	−0.37	−22.01	40.23	16.77	50.62	−12.91	21.06
cc-pv5z	−122.59	1.54	−459.71	95.93	43.31	194.5	−281.72	171.32
sadlej	15.86	85.9	28.96	10.64	0.65	33.3	−18.07	27.63
sadlej+	3.15	95.29	1.09	40.75	0.24	36.24	0.29	25.29

<sup>a</sup> Mean absolute shift (eV).

one superior basis set. The aug-cc-pv5z basis gives the lowest total energy and lowest MAS, which is perhaps no surprise since it is more complete than the other basis sets. The sadlej and sadlej+ basis sets also gave reasonable results.

#### 4.1.2. Convergence of orbital energies with respect to basis set

All the calculations with the different basis sets agree on the ordering of the occupied orbitals and the magnitude of their orbital energies. But a similar statement can not be made for the virtual orbitals where, for example, the lowest unoccupied molecular orbital (LUMO) of C<sub>2</sub>H<sub>4</sub> will be of different symme-

try and orbital energy for basis sets that are often believed to be fairly complete like aug-cc-pv5z, cc-pv5z or cc-pv5z-d (cc-pv5z with added *d* functions). Such differences are expected because of the aforementioned difficulties establishing the precise very large *r* behavior with the present OEP method. Clearly this will require a more complete investigation. Examples of energy and ordering of orbitals are given for H<sub>2</sub>O and C<sub>2</sub>H<sub>4</sub> in Tables 2 and 3. Note that the interchange of the orbitals 5*a*<sub>1</sub> and 2*b*<sub>1</sub> of H<sub>2</sub>O (Table 2) corresponds very well to the lack of any obvious convergence in their orbital energies. This is also true in the case of C<sub>2</sub>H<sub>4</sub> (Table 3).

#### 4.1.3. Orbital convergence with respect to basis set

While in some cases, the 1*b*<sub>2</sub> orbital of H<sub>2</sub>O for example, the choice of orbital basis set does not have much impact, in other cases, the 2*a*<sub>1</sub> orbital of H<sub>2</sub>O for example, we have a clear estimate of difficulties describing the very large *r* behavior as a function of the orbital basis set. This appears to be an extreme case with most MDs being less sensitive to choice of basis set. In particular Fig. 2 shows that there seems to be some tendency for basis set convergence problems at large *r* (low *p*) to be more hidden by spherical averaging in p-type rather than s-type MDs. This is also apparent in the MDs of RIHF orbitals.

#### 4.2. Errors due to the resolution-of-the-identity approximation

Resolution-of-the-identity techniques allow us to eliminate all four-center electron repulsion integrals from our calculations while introducing errors no larger than about 0.05 eV in the HF orbital energies of molecules involving only first-row elements to

Table 2

Energy (eV) and ordering of the OEP orbitals of H<sub>2</sub>O for various basis sets

	sadlej	sadlej+	cc-pv5z	aug-cc-pv5z
HOMO	−31.98	−31.97	−32.02	−32.02
LUMO	−19.31	−19.31	−19.24	−19.23
	−15.82	−15.82	−15.77	−15.76
	−13.85	−13.85	−13.80	−13.81
	−5.40	−5.44	−5.25	−5.28
	−3.30	−3.28	−2.80	−2.98
	−2.57	−2.21	0.34	−2.09
	−2.29	−2.08	1.19	−1.75
HOMO	2 <i>a</i> <sub>1</sub>	2 <i>a</i> <sub>1</sub>	2 <i>a</i> <sub>1</sub>	2 <i>a</i> <sub>1</sub>
LUMO	1 <i>b</i> <sub>2</sub>	1 <i>b</i> <sub>2</sub>	1 <i>b</i> <sub>2</sub>	1 <i>b</i> <sub>2</sub>
	3 <i>a</i> <sub>1</sub>	3 <i>a</i> <sub>1</sub>	3 <i>a</i> <sub>1</sub>	3 <i>a</i> <sub>1</sub>
	1 <i>b</i> <sub>1</sub>	1 <i>b</i> <sub>1</sub>	1 <i>b</i> <sub>1</sub>	1 <i>b</i> <sub>1</sub>
	4 <i>a</i> <sub>1</sub>	4 <i>a</i> <sub>1</sub>	4 <i>a</i> <sub>1</sub>	4 <i>a</i> <sub>1</sub>
	2 <i>b</i> <sub>2</sub>	2 <i>b</i> <sub>2</sub>	2 <i>b</i> <sub>2</sub>	2 <i>b</i> <sub>2</sub>
	5 <i>a</i> <sub>1</sub>	2 <i>b</i> <sub>1</sub>	5 <i>a</i> <sub>1</sub>	2 <i>b</i> <sub>1</sub>
	2 <i>b</i> <sub>1</sub>	5 <i>a</i> <sub>1</sub>	2 <i>b</i> <sub>1</sub>	5 <i>a</i> <sub>1</sub>

Table 3  
Energy (eV) and ordering of the OEP orbitals of C<sub>2</sub>H<sub>4</sub> for various basis sets

	sadlej	sadlej +	cc-pv5z	aug-cc-pv5z	cc-pv5z-d
HOMO	−22.63	−22.66	−22.74	−22.77	−22.77
LUMO	−17.90	−17.93	−18.00	−18.04	−18.03
	−15.08	−15.12	−15.13	−15.18	−15.17
	−13.94	−13.97	−13.95	−13.99	−13.97
	−12.34	−12.36	−12.32	−12.36	−12.32
	−10.23	−10.23	−10.19	−10.2	−10.20
	−4.10	−4.11	−4.09	−6.59	−4.16
	−2.78	−2.86	−3.30	−5.5	−2.41
	−1.83	−2.04	−2.77	−4.15	−1.72
	−1.35	−1.65	−1.86	−3.8	−1.54
	−1.31	−1.38	−1.38	−2.96	−0.44
	−0.81	−0.91	−0.57	−2.48	−0.26
HOMO	2a <sub>g</sub>	2a <sub>g</sub>	2a <sub>g</sub>	2a <sub>g</sub>	2a <sub>g</sub>
LUMO	2b <sub>1u</sub>	2b <sub>1u</sub>	2b <sub>1u</sub>	2b <sub>1u</sub>	2b <sub>1u</sub>
	1b <sub>3u</sub>	1b <sub>3u</sub>	1b <sub>3u</sub>	1b <sub>3u</sub>	1b <sub>3u</sub>
	3a <sub>g</sub>	3a <sub>g</sub>	3a <sub>g</sub>	3a <sub>g</sub>	3a <sub>g</sub>
	1b <sub>2g</sub>	1b <sub>2g</sub>	1b <sub>2g</sub>	1b <sub>2g</sub>	1b <sub>2g</sub>
	1b <sub>2u</sub>	1b <sub>2u</sub>	1b <sub>2u</sub>	1b <sub>2u</sub>	1b <sub>2u</sub>
	1b <sub>3g</sub>	1b <sub>3g</sub>	1b <sub>3g</sub>	3b <sub>1u</sub>	1b <sub>3g</sub>
	4a <sub>g</sub>	4a <sub>g</sub>	3b <sub>1u</sub>	2b <sub>2g</sub>	4a <sub>g</sub>
	2b <sub>3u</sub>	2b <sub>3u</sub>	2b <sub>2g</sub>	1b <sub>3g</sub>	3b <sub>1u</sub>
	3b <sub>1u</sub>	3b <sub>1u</sub>	4a <sub>g</sub>	2b <sub>3u</sub>	2b <sub>3u</sub>
	2b <sub>2u</sub>	2b <sub>2u</sub>	2b <sub>3u</sub>	4a <sub>g</sub>	2b <sub>2g</sub>
	5a <sub>g</sub>	5a <sub>g</sub>	5a <sub>g</sub>	5a <sub>g</sub>	2b <sub>2u</sub>

judge by our earlier tests [38].

The effect of this approximation on the momentum distribution can be seen in Fig. 3 for the 5σ orbital of CO where the difference between the HF and RIHF curves is only barely visible.

#### 4.3. Orbital energies and experimental ionization potentials

Over 100 vertical ionization potentials were computed with DFT using the exchange-only optimized effective potential.

Tables 4, 5 and 6 summarize the vertical ionization potentials computed with various methods and the experimental ones for a set of 22-electron molecules. Tables 7 and 8 summarize the vertical ionization potentials computed with various methods and the experimental ones for a set of small molecules.

One can readily see in Fig. 4 that the exchange-

only OEP method gives very good ionization potentials. The mean absolute difference (MAD) between experimental ionization potentials and calculated ones is given in Table 9. Also included in the table are results from the pGF2 method. This is a simple semiempirical approximation of an ab initio Green function method which is of comparable computational complexity to the OEP calculation carried out here and yet gives better results, on average, for ionization potentials [48] and also encouraging results for EMS MDs [50]. It can be further simplified to the pGW2 approximation [51]. (See also Ref. [52] for a very recent investigation of GW approximations for molecular ionization potentials). OEP results have a MAD about only twice that of pGF2 and less than half that of Hartree–Fock.

Koopmans' theorem gives the wrong ordering for the HOMO of CH<sub>3</sub>NC, the 3σ<sub>g</sub> of F<sub>2</sub>, 3b<sub>2</sub> and 1b<sub>1</sub> of F<sub>2</sub>O, 1a'' of HN<sub>3</sub>, the HOMO of N<sub>2</sub>. It is interesting



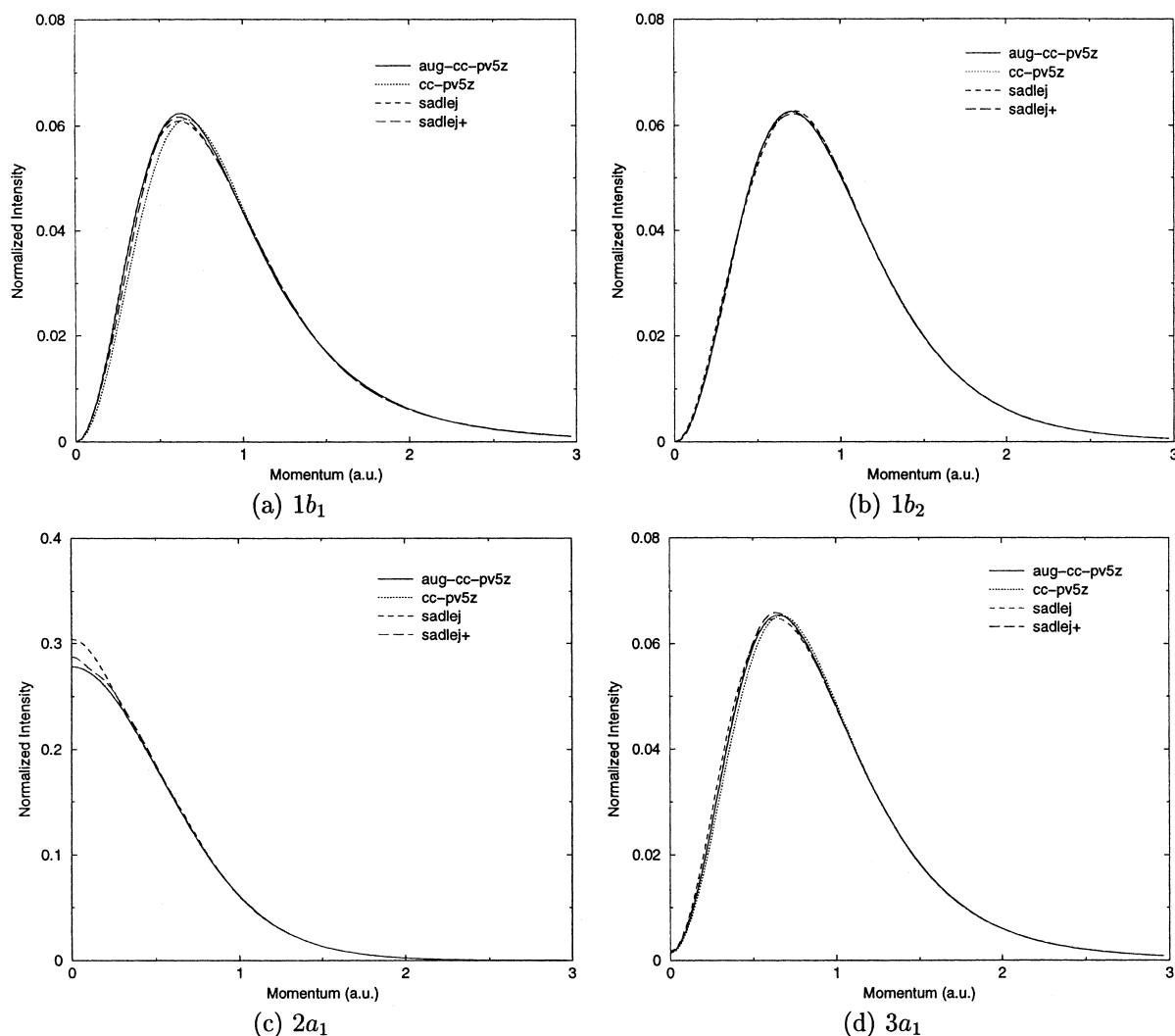


Fig. 2. MD of four orbitals of  $\text{H}_2\text{O}$ . OEP results with various orbital basis sets.

to note that this is corrected by the OEP local exchange potential. As pointed out by Garza et al. [53], the fact that a local exchange-only method corrects the ordering of states means that to this end, the nature of the exchange potential is more important than an adequate treatment of the correlation.

However, this is not always the case as the ordering of state  $7\sigma$  of the FCCH molecule is just as wrong in HF and in OEP. Clearly, for this molecule, the locality of the exchange potential is not enough and some treatment of correlation has to be included. LDA gets the ordering right in this case, while giving

the wrong ordering for the  $6a_1$  of  $\text{F}_2\text{O}$  and the HOMO of HCN. Note that it is not surprising that the LDA gets the ordering of the IPs correct when the HF and OEP gets it wrong for FCCH. Within a given molecule, the LDA orbital energies tend to look like shifted OEP orbital energies, *except* when correlation is important, in which case, the LDA orbital energies look more like shifted-IPs, instead of shifted OEP energies. Interestingly enough, all three methods give the wrong ordering for the  $1a''$  and  $9a'$  of  $\text{H}_2\text{NCN}$ .

Note that in the particular case the HF and OEP

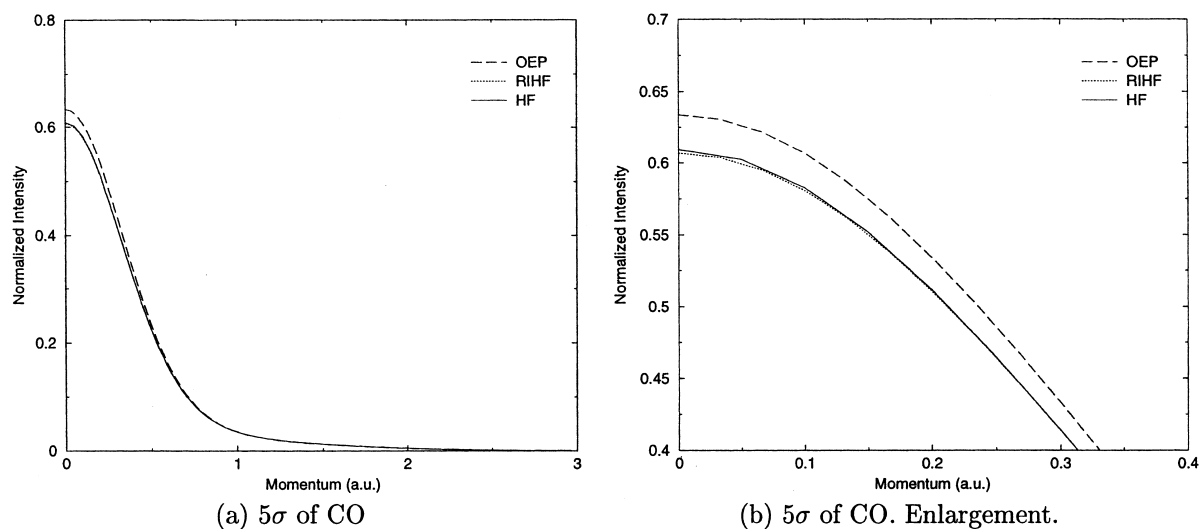


Fig. 3. MD of 5σ orbital of CO. OEP, RIHF and HF results.

Table 4

Difference between experimental and calculated ionization potentials (orbital energies) for 22 electrons molecules for various methods

Molecule	Orbital	Expt. <sup>a</sup>	Expt.-			
			pGF2 <sup>b</sup>	OEP	HF	LDA
Allene	4a <sub>1</sub>	17.30	-0.71	0.48	-2.16	4.49
	3b <sub>2</sub>	14.75	-1.06	-0.38	-2.32	3.66
	1e	14.75	-0.72	-0.06	-1.79	3.80
	2e	10.02	0.05	-0.27	-0.29	3.33
CH <sub>3</sub> CCH	6a <sub>1</sub>	17.20	-0.93	0.19	-2.37	4.27
	7a <sub>1</sub>	15.50	-0.10	0.31	-1.41	4.34
	1e	14.40	-0.81	-0.28	-1.58	3.81
	2e	10.37	0.04	-0.05	-0.07	3.76
Cyclopropene	4a <sub>1</sub>	19.60		1.04	-2.88	4.93
	2b <sub>1</sub>	18.30	-0.93	0.70	-2.66	4.41
	5a <sub>1</sub>	16.68	-0.60	0.64	-1.85	4.24
	1b <sub>2</sub>	15.09	-0.26	0.73	-1.15	4.34
	6a <sub>1</sub>	12.70	0.14	0.46	-0.67	4.20
	3b <sub>1</sub>	10.89	0.08	-0.06	-0.57	3.63
	2b <sub>2</sub>	9.86	0.26	0.13	0.14	3.64
CH <sub>3</sub> CN	6a <sub>1</sub>	17.40	-0.21	0.09	-1.54	4.63
	1e	15.50	-0.90	-0.64	-1.53	4.01
	7a <sub>1</sub>	13.11	-0.09	-0.62	-2.02	4.52
	2e	12.18	-0.19	-0.35	-0.36	3.93
CH <sub>3</sub> NC	1e	16.14	-0.50	-2.93	-3.33	2.37
	2e	12.46	-0.01	-0.73	0.33	4.44
	7a <sub>1</sub>	11.24	-0.60	-1.38	-1.39	4.16
FCCH	7σ	18.00	-0.58	0.49	-1.79	4.85
	1π	17.80	-0.18	-0.72	-2.87	4.97
	2π	11.26	-0.01	-0.12	-0.12	4.10

Units are in eV.

<sup>a</sup> Experimental values taken from [DC93].<sup>b</sup> pGF2 results taken from Ref. [48].

Table 5

Difference between experimental and calculated ionization potentials (orbital energies) for 22 electrons molecules for various methods

Molecule	Orbital	Expt. <sup>a</sup>	Expt.-			
			pGF2 <sup>b</sup>	OEP	HF	LDA
FCN	6 $\sigma$	22.60		−0.38	−2.75	5.12
	1 $\pi$	19.30		−0.96	−2.88	5.19
	7 $\sigma$	14.56	0.03	−0.35	−1.79	4.98
	2 $\pi$	13.65	0.15	0.01	0.00	4.75
HCNO	6 $\sigma$	19.10		−0.08	−3.59	4.09
	7 $\sigma$	17.79	0.43	0.08	−2.26	4.53
	1 $\pi$	15.92	−0.34	−0.29	−2.61	3.51
	2 $\pi$	10.83	0.45	−0.27	−0.29	3.94
NNO	6 $\sigma$	20.11		0.04	−2.61	5.13
	1 $\pi$	18.23	−0.55	−0.18	−2.55	4.03
	7 $\sigma$	16.38	−0.55	−0.22	−2.64	4.88
	2 $\pi$	12.89	0.22	−0.47	−0.49	4.31
HN <sub>3</sub>	6a'	20.10		−0.15	−3.12	3.89
	1a''	17.40	0.04	1.03	−1.78	4.46
	7a'	16.70	−0.69	0.37	−2.51	3.88
	8a'	15.47	−0.81	−0.03	−2.91	4.40
	9a'	12.20	0.09	0.11	−0.55	4.12
	2a''	10.70	0.17	−0.26	−0.29	3.71
HNCO	6a'	19.24		−1.19	−3.74	3.41
	7a'	17.50	−0.15	−0.07	−2.40	5.06
	1a''	15.80	−0.43	−0.25	−1.98	4.24
	8a'	15.80	−0.34	−0.12	−1.83	4.25
	9a'	12.30	0.16	−0.36	−0.48	4.43
	2a''	11.62	1.07	−0.71	−0.73	4.04

Units are in eV.

<sup>a</sup> Experimental values taken from [DC93].<sup>b</sup> pGF2 results taken from Ref. [48].

HOMO are of different symmetry, one fixes the potential shift by first identifying the HOMO in the OEP calculation with the help of the Aufbau principle. It is then not a problem to enforce the condition  $\epsilon_{\text{HOMO}}^{\text{OEP}} = \epsilon_{\text{HOMO}}^{\text{HF}}$  since  $\epsilon_{\text{HOMO}}^{\text{HF}}$  is evaluated with the OEP orbitals.

Koopmans' theorem is so well-known in Hartree–Fock that it hardly needs comment. It works primarily because the neglect of relaxation effects raises the ionization potential while the neglect of electron correlation lowers the ionization potential, so that errors due to neglecting these two important physical effects tend to cancel. In DFT, there is a Kohn–Sham analogue to Koopmans' theorem for occupied

orbital energies, but it works entirely differently. As mentioned earlier, the HOMO energy is well-known to become the negative of the ionization potential when the exchange–correlation functional is exact and a similar statement may be made regarding other Kohn–Sham energies. This is because Kohn–Sham orbital energy differences provide a first approximation to excitation energies [CS00]. In essence, this is because, in contrast to the Hartree–Fock case, Kohn–Sham occupied and unoccupied orbitals “see” the same potential and hence the same number of electrons. They are thus preprepared to describe excitations which leave the charge density (and hence the exchange–correlation potential) largely

Table 6

Difference between experimental and calculated ionization potentials (orbital energies) for 22 electrons molecules for various methods

Molecule	Orbital	Expt. <sup>a</sup>	Expt.-			
			pGF2 <sup>b</sup>	OEP	HF	LDA
CH <sub>2</sub> CO	6a <sub>1</sub>	18.20	−0.07	0.65	−2.51	4.92
	7a <sub>1</sub>	16.80	−0.39	0.59	−1.75	4.51
	1b <sub>2</sub>	16.30	−0.58	0.44	−1.64	4.24
	1b <sub>1</sub>	15.00	−0.55	−0.23	−2.50	3.79
	2b <sub>2</sub>	14.20	−0.23	0.19	−1.16	3.99
	2b <sub>1</sub>	9.80	0.21	−0.20	−0.22	3.74
Diazirine	4a <sub>1</sub>	21.50		0.17	−3.63	4.61
	2b <sub>1</sub>	20.30		0.54	−2.85	5.30
	1b <sub>2</sub>	17.50	−0.17	0.52	−1.04	4.52
	5a <sub>1</sub>	16.50	−0.27	−0.06	−1.56	4.18
	6a <sub>1</sub>	14.15	−0.26	−0.34	−1.71	4.42
	2b <sub>2</sub>	13.25	0.21	0.25	−0.02	4.38
	3b <sub>1</sub>	10.75	0.17	−0.48	−0.52	3.88
Diazomethane	6a <sub>1</sub>	18.50	−0.39	1.09	−2.20	4.72
	1b <sub>2</sub>	16.93	−0.69	0.69	−2.03	3.78
	1b <sub>1</sub>	16.93	0.86	2.04	−0.97	4.94
	7a <sub>1</sub>	15.13	−0.50	0.50	−2.69	4.36
	2b <sub>2</sub>	14.13	−0.09	0.95	−0.62	4.11
	2b <sub>1</sub>	9.00	0.22	0.03	0.01	3.39
H <sub>2</sub> NCN	6a'	19.60	−0.87	−1.09	−3.47	3.20
	1a''	18.80	−0.41	4.43	3.15	8.72
	7a'	14.23	−0.15	−3.48	−5.10	0.88
	8a'	12.98	−0.23	−0.27	−2.13	4.47
	2a''	12.50	−0.04	1.43	1.42	5.82
	9a'	10.65	−0.06	−1.46	−1.74	2.58

Units are in eV.

<sup>a</sup> Experimental values taken from [DC93].<sup>b</sup> pGF2 results taken from Ref. [48].

unchanged. More rigorous reasoning (within the two-level model and the Tamm–Dancoff approximation) shows that Kohn–Sham orbital energy differences lie between the corresponding singlet and triplet excitation energies for closed shell molecules [CS00]. For excitations to Rydberg states, the singlet–triplet splitting becomes small so that the orbital energy difference becomes an excellent approximation when a sufficiently good Kohn–Sham potential is used. Since ionization may be regarded as an extreme example of excitation to a diffuse (really a continuum) orbital, we should expect the true Kohn–Sham orbital energies to behave like ionization energies. Note also that the OEP results are invariant

under unitary transformations by construction since the HF operator whose expectation value is taken is explicitly invariant under unitary transformation of the occupied orbitals.

#### 4.4. OEP momentum distributions

In order to test the quality of the momentum distribution of exchange-only OEP orbitals, we compare results with LDA, Becke's 1988 exchange functional [B88] plus Perdew's 1986 correlation functional [P86] (BP) and configuration interaction (CI) results of Duffy et al. [13] for six small molecules (C<sub>2</sub>H<sub>2</sub>, CO, CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O and HF)

Table 7

Difference between experimental and calculated ionization potentials (orbital energies) for small molecules for various methods

Molecule	Orbital	Expt. <sup>a</sup>	Expt.-			
			pGF2 <sup>b</sup>	OEP	HF	LDA
F <sub>2</sub> O	3b <sub>2</sub>	20.90		−1.22	−0.94	4.73
	5a <sub>1</sub>	19.50	0.21	−1.99	−2.38	4.92
	1b <sub>1</sub>	18.68	−0.08	−2.46	−3.66	5.28
	1a <sub>2</sub>	16.47	−0.16	−2.74	−3.24	5.39
	4b <sub>2</sub>	16.32	0.05	−2.55	−2.24	5.51
	6a <sub>1</sub>	16.17	−0.23	−2.42	−1.73	4.97
F <sub>2</sub>	2b <sub>1</sub>	13.26	−0.16	−2.66	−2.64	5.45
	3a <sub>g</sub>	21.00		−0.94	0.43	5.17
	1b <sub>2u</sub>	18.80	0.01	−2.53	−3.32	5.74
CH <sub>2</sub> O	1b <sub>3g</sub>	15.83	0.21	−2.39	−2.39	6.20
	4a <sub>1</sub>	21.40		0.84	−2.21	5.76
	1b <sub>2</sub>	17.00	−0.28	−0.14	−1.81	4.79
	5a <sub>1</sub>	16.10	0.13	−0.44	−1.66	4.98
	1b <sub>1</sub>	14.50	0.31	−0.38	−0.12	4.19
C <sub>2</sub> H <sub>2</sub>	2b <sub>2</sub>	10.90	0.19	−1.13	−1.15	4.58
	2σ <sub>g</sub>	23.50		0.19	−4.65	4.91
	2σ <sub>u</sub>	18.70	−0.73	0.35	−2.24	4.66
	3σ <sub>g</sub>	16.70	−0.70	0.06	−1.83	4.49
CO	1π <sub>u</sub>	11.49	0.23	0.30	0.30	4.16
	4σ	19.72	0.10	−1.08	−2.20	5.52
	1π	16.91	0.09	−0.65	−0.50	4.83
	5σ	14.01	−0.43	−1.13	−1.12	4.91

Units are in eV.

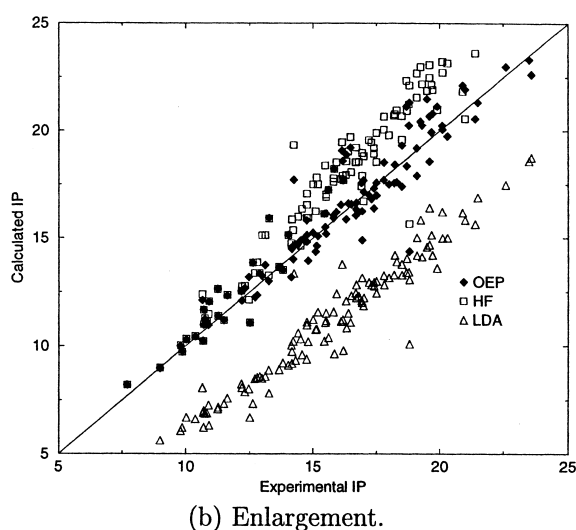
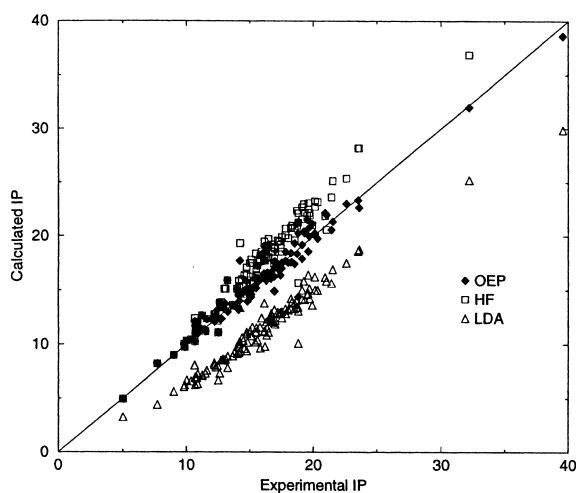
<sup>a</sup> Experimental values taken from [DC93].<sup>b</sup> pGF2 results taken from Ref. [48].

Fig. 4. Correlation graph of calculated IPs and experimental ones for all the molecules in the tables. Units are in eV.

Table 8

Difference between experimental and calculated ionization potentials (orbital energies) for small molecules for various methods

Molecule	Orbital	Expt. <sup>a</sup>	Expt.-			
			pGF2 <sup>b</sup>	OEP	HF	LDA
HCN	4 $\sigma$	19.68	-1.26	-0.25	-2.47	4.56
	5 $\sigma$	14.15	0.17	-0.41	-1.70	4.96
	1 $\pi$	13.80	0.19	0.28	0.28	4.59
N <sub>2</sub>	2 $\sigma_u$	18.78	-0.39	-1.46	-2.47	5.37
	1 $\pi_u$	16.98	-0.01	-0.70	0.27	5.14
	3 $\sigma_g$	15.60	-0.27	-1.64	-1.65	5.24
H <sub>2</sub> O	2a <sub>1</sub>	32.20		0.22	-4.65	7.00
	1b <sub>2</sub>	18.51	6.27	-0.80	-1.08	5.23
	3a <sub>1</sub>	14.74	0.19	-1.08	-1.18	5.37
	1b <sub>1</sub>	12.62	-6.01	-1.23	-1.23	5.29
HF	2 $\sigma$	39.58		0.98	-4.05	9.71
	3 $\sigma$	19.90	0.26	-1.24	-1.08	6.31
	1 $\pi$	16.19	0.41	-1.51	-1.51	6.42
C <sub>2</sub> H <sub>4</sub>	2a <sub>g</sub>	23.59 <sup>c</sup>		0.96	-4.55	4.85
	2b <sub>1u</sub>	19.10 <sup>c</sup>		1.20	-2.47	4.91
	1b <sub>3u</sub>	15.18 <sup>c</sup>		0.10	-2.33	3.64
	3a <sub>g</sub>	14.80 <sup>c</sup>		0.87	-1.11	4.63
	1b <sub>2g</sub>	12.79 <sup>c</sup>		0.44	-1.07	4.25
	1b <sub>2u</sub>	10.68 <sup>c</sup>		0.45	0.46	3.77
CH <sub>4</sub>	1t <sub>2</sub>	-14.30		-0.38	-0.38	4.97
NH <sub>3</sub>	3a <sub>1</sub>	-10.70		-0.96	-0.96	4.48
H <sub>2</sub>	1a <sub>g</sub>	-15.43		-0.70	-0.70	5.22
Li <sub>2</sub>	2a <sub>g</sub>	-5.00		0.05	0.05	1.74
LiH	2a <sub>1</sub>	-7.70		-0.51	-0.51	3.31

Units are in eV.

<sup>a</sup> Experimental values taken from [DC93].

<sup>b</sup> pGF2 results taken from Ref. [48].

<sup>c</sup> Experimental values taken from [BA80].

selected because their EMS has been well studied both experimentally and theoretically. All OEP calculations were done with the aug-cc-pv5z basis set used by Duffy et al.

The positions and overall shapes of the MDs obtained with the various methods are all similar, the difference between them being mostly in the height of the peaks. Although orbital energies dictate the

asymptotic behavior of the orbitals, the better orbital energies provided by the OEP method compared to Hartree–Fock do not appear to contribute much to the improvement of the MDs, except maybe for the HOMO of the CO molecule (Fig. 5a) where the OEP MD is identical to the CI one. In other cases (Figs. 5b–7d) the OEP MDs follow closely the Hartree–Fock MDs and this either leads to somewhat better or somewhat worse results than LDA or BP orbitals, depending on whether Hartree–Fock more closely approximated the CI result or not. One exception is the 2a<sub>1</sub> orbital of NH<sub>3</sub> where the CI, RIHF and BP curves are very close and where the OEP curve has a lower peak intensity.

That the OEP MDs follow closely the Hartree–Fock MDs is not too surprising as one of the early OEP papers of Talman [57] showed that Hartree–Fock and OEP Compton profiles are essentially identical, a Compton profile being more or less the sum of all the EMS MDs over all the orbitals of the molecule. Yet while we expect the OEP orbitals to look a lot like HF orbitals, it is possible that the OEP orbitals do not resemble *canonical* HF orbitals, but rather some unitary transformation among occupied HF orbitals. If this is true, orbitals such as 1b<sub>1</sub> (Fig. 5f) and 1b<sub>2</sub> (Fig. 6a) of H<sub>2</sub>O which are the unique occupied orbitals belonging to their symmetry representation would be essentially unrotated, while the 1a<sub>1</sub>, 2a<sub>1</sub> (Fig. 6c), and 3a<sub>1</sub> (Fig. 6d) could be rotated among themselves [58]. This does not appear to be the case for H<sub>2</sub>O, NH<sub>3</sub> or HF (Fig. 7) as all these OEP and HF MDs are very similar.

While the locality of the exchange potential was important to get the right ordering of the states, it appears not to have much incidence on the overall shape of the MD since exchange-only OEP and HF MDs are so close. Hence the correlation contribution will have to be taken into account in order to test if DFT MDs more closely approximate CI or HF results for this type of electronic property.

The comparison of the exact exchange (OEP) and of the LDA approximations allows us to understand better the effect of the large *r* behavior of the Kohn–Sham orbitals on the shape and height of the MDs. Clearly, the shape of the MDs does not appear to be much influenced by large *r* behavior but height appears to be.

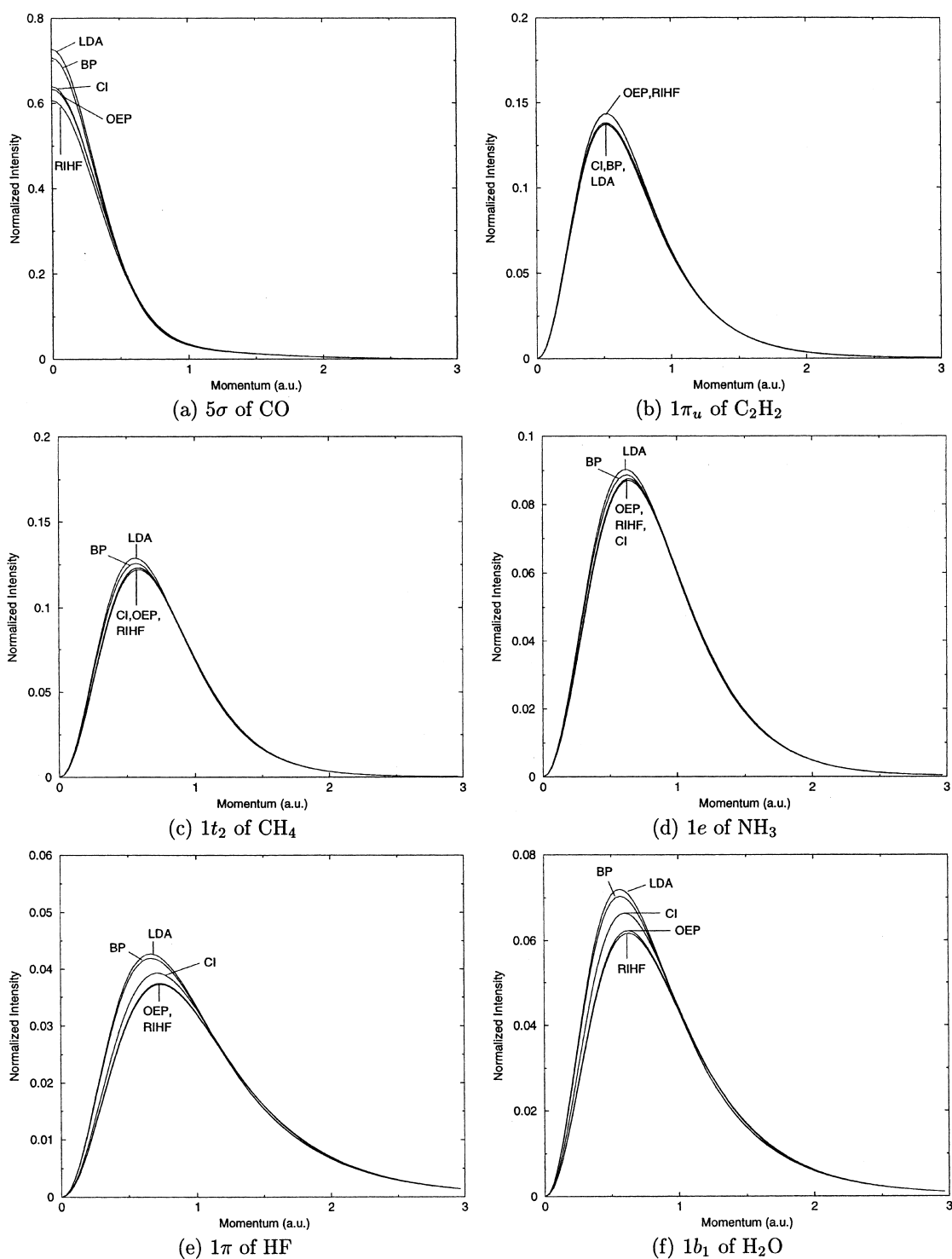


Fig. 5. Momentum distribution of HOMO orbitals of six molecules obtained with various methods.

Table 9

Mean absolute difference (eV) between experimental ionization potentials and calculated ones

Method	pGF2	LDA	HF	OEP
MAD	0.34	4.56	1.76	0.76

## 5. Conclusion

Since the seminal work of Duffy et al. [13], DFT has been widely adopted by the EMS community as a useful source of orbitals for comparison against

experimentally determined momentum profiles. Though there is some formal justification as to why this might be a good approximation [13,20], the primary justification has been that theoretical spherically averaged momentum distributions for Kohn–Sham DFT orbitals calculated using *approximate* exchange-correlation functionals compare well with experimental momentum profiles. In some cases [59] DFT actually seems to do better than sophisticated configuration interaction calculations since DFT provides more diffuse orbitals whose MDs are in better agreement with the measured EMS XMPs. A

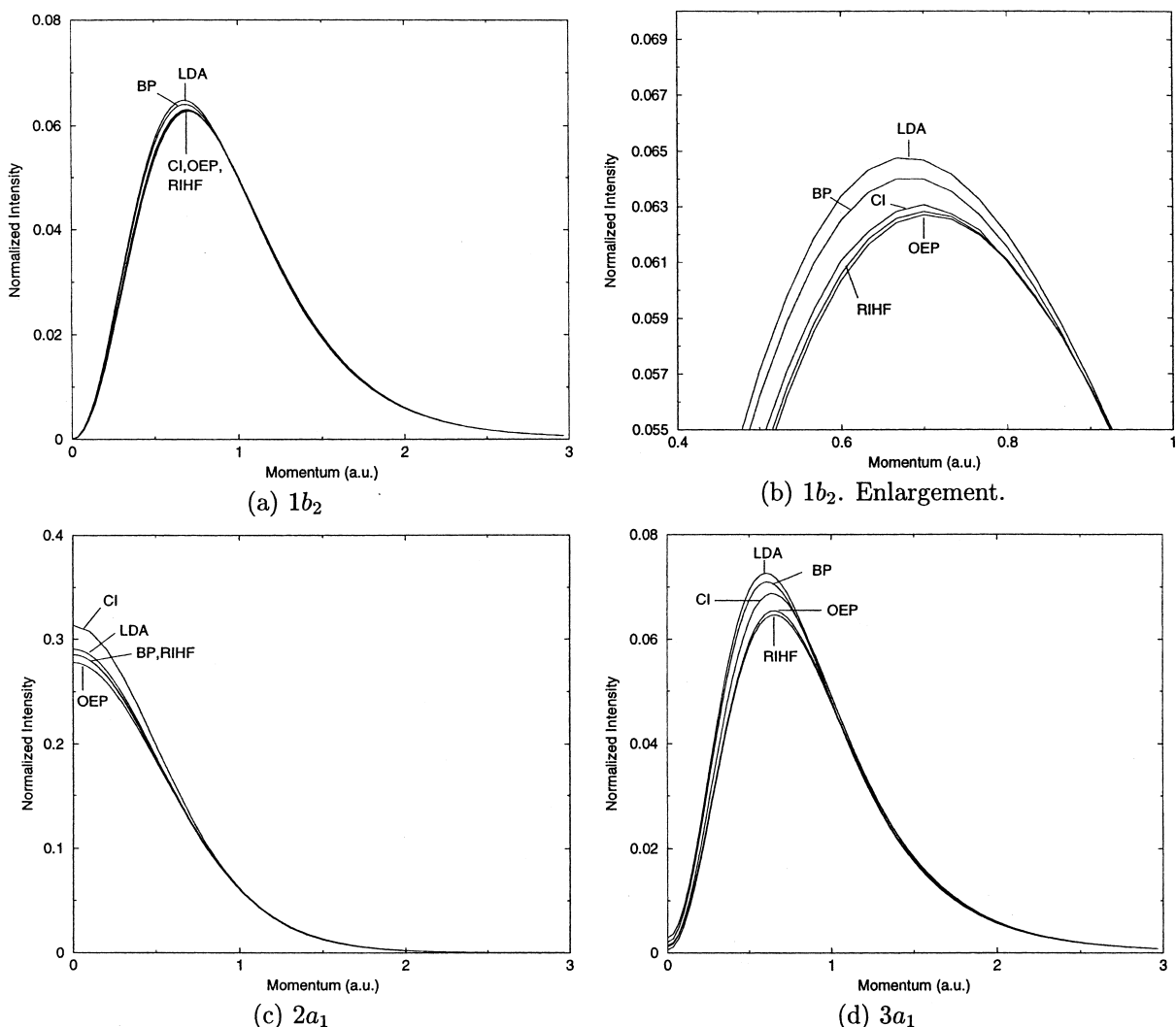


Fig. 6. Momentum distribution of orbitals other than HOMO of H<sub>2</sub>O obtained with various methods.



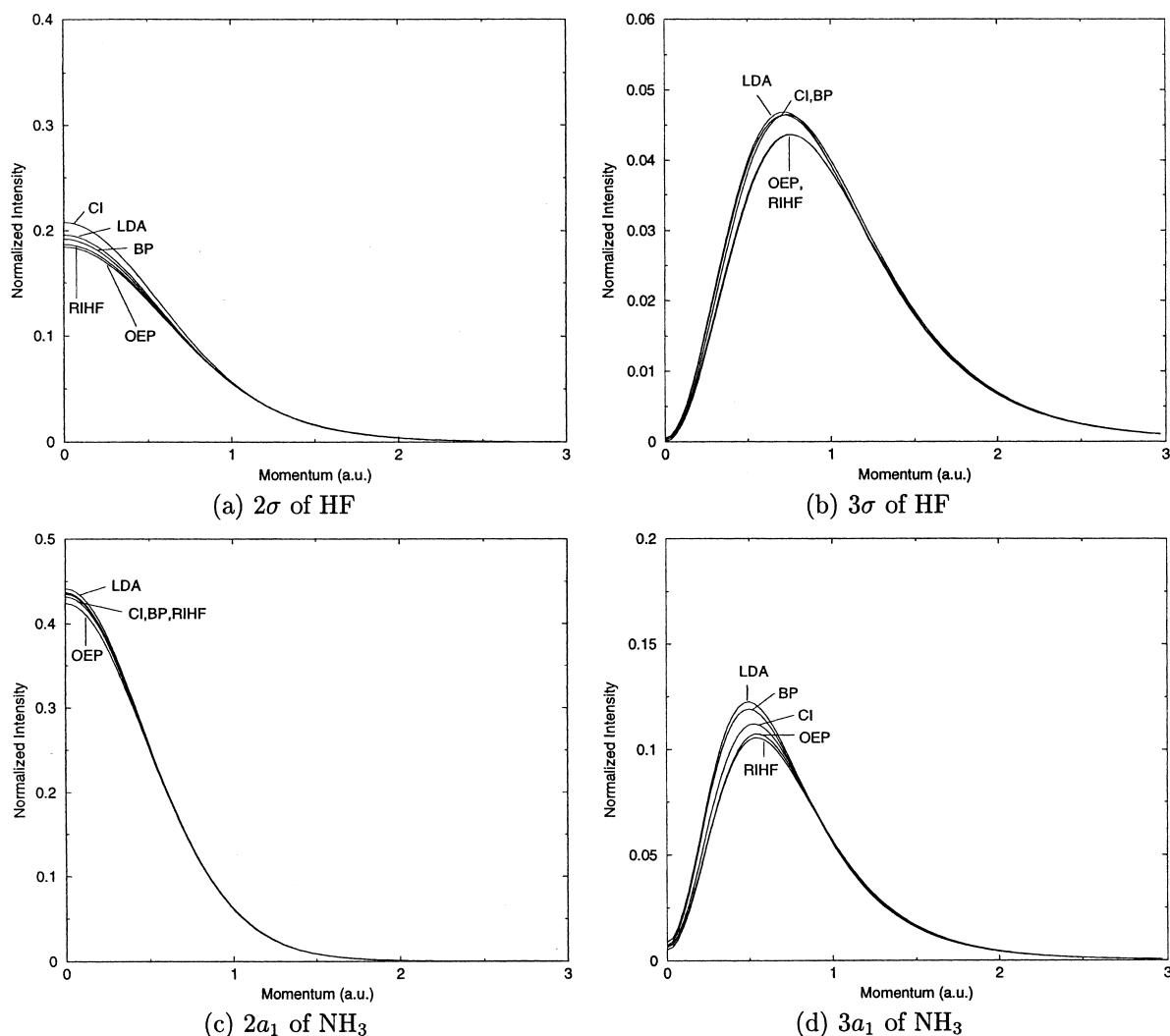


Fig. 7. Momentum distribution of orbitals other than HOMO of HF and NH<sub>3</sub> obtained with various methods.

disturbing thought is that this may not actually be a success of DFT as such, but rather an artifact of the known underbinding of electrons by approximate exchange-correlation potentials. The only way to really test this is to see what happens when an exact (or nearly exact) xc potential is used. In this article, we have come closer to realizing this crucial test for EMS applications of DFT in that we have calculated essentially exact exchange-only DFT orbitals and orbital energies and analyzed their significance for ionization phenomena.

We find that the resultant DFT MDs are *virtually identical* to the corresponding HF MDs, and are much less diffuse than DFT MDs calculated with approximate functionals. Since correlation often has only a small effect on MDs, we feel that this is strong evidence that the previously found good agreement between DFT MDs and EMS XMPs was partially due to known errors in the approximate exchange-correlation potentials used in the DFT calculations. On the other hand, our results do coincide nicely with the idea that Kohn–Sham

orbitals should be good approximations to Dyson orbitals, because Dyson orbitals are just canonical Hartree–Fock orbitals when correlation is neglected.

A question posed in the initial work of Duffy et al. [13] was how DFT orbitals could yield such good ionization cross-sections while DFT orbital energies seemed to have little to do with experimentally determined ionization potentials. Indeed, the commonly held view among quantum chemists is that DFT orbital energies are formally meaningless. Nevertheless there is some indication that at least many aficionados of DFT recognize that shifted orbital energies provide excellent first approximations to experimental IPs [60–62]. In this article, we have actually shown that Koopmans' theorem works *better* in exact exchange-only DFT than it does in Hartree–Fock when it comes to approximating experimental ionization potentials.

We feel that the results given in this paper provide further support for the argument that DFT orbitals and orbital energies are more than just an artificial construct. In fact, they provide a useful approximation for ionization processes in molecules.

## Acknowledgements

Financial support through grants from the Natural Sciences and Engineering Research Council (NSERC) of Canada, the Canadian Institute for Photonics Innovation (CIPI), and the Fonds pour la Formation des Chercheurs et l'Aide à la Recherche (FCAR) of Québec is gratefully acknowledged. P.D. and M.E.C. would like to thank Professor Chris Brion for his introduction to and infectious enthusiasm for EMS.

## References

- [1] J. Rolke, Y. Zheng, C.E. Brion, Y.A. Wang, E.R. Davidson, *Chem. Phys.* 230 (1998) 153.
- [2] X.W. Fan, X.J. Chen, S.J. Zhou, Y. Zheng, C.E. Brion, R. Frey, E.R. Davidson, *Chem. Phys. Lett.* 276 (1999) 346.
- [3] J. Rolke, Y. Zheng, S.J. Chakrovorty, E.R. Davidson, I.E. McCarthy, *Chem. Phys.* 215 (1997) 191.
- [4] Y. Zheng, C.E. Brion, M. Brunger, K. Zhao, A.M. Grisogono, S. Braidwood, E. Weigold, E.R. Davidson, A. Sgamellotti, W. von Niessen, *Chem. Phys.* 212 (1996) 269–300.
- [5] J. Rolke, N. Cann, Y. Zheng, B.P. Hollebone, C.E. Brion, Y.A. Wang, E.R. Davidson, *Chem. Phys.* 201 (1995) 1.
- [6] B.P. Hollebone, J.J. Neville, Y. Zheng, C.E. Brion, Y. Wang, E.R. Davidson, *Chem. Phys.* 196 (1995) 13–35.
- [7] Y. Zheng, J.J. Neville, C.E. Brion, Y. Wang, E.R. Davidson, *Chem. Phys.* 188 (1994) 109.
- [8] B.P. Hollebone, P. Duffy, C.E. Brion, Y. Wang, E.R. Davidson, *Chem. Phys.* 178 (1993) 25–38.
- [9] B.P. Hollebone, C.E. Brion, E.R. Davidson, C. Boyle, *Chem. Phys.* 173 (1993) 193.
- [10] A.O. Bawagan, C.E. Brion, E.R. Davidson, D. Feller, *Chem. Phys.* 113 (1987) 19, and references therein.
- [11] J.K. Deng et al., *J. Chem. Phys.* 114 (2001) 882.
- [12] M.J. Brunger, D.A. Winkler, M.T. Michalewicz, E. Weigold, *J. Chem. Phys.* 108 (1997) 1859.
- [13] P. Duffy, D.P. Chong, M.E. Casida, D.R. Salahub, *Phys. Rev. A* 50 (1994) 4707.
- [14] C.E. Brion, G. Cooper, Y. Zheng, I.V. Litvinyuk, I.E. McCarthy, *Chem. Phys.* 270 (2001) 13.
- [15] A.D. Becke, *Phys. Rev. A* 33 (1996) 2786.
- [16] I.E. McCarthy, E. Weigold, *Rept. Prog. Phys.* 51 (1988) 319, and references therein.
- [17] C.E. Brion, in: T. Anderson et al. (Ed.), *The Physics of Electronic and Atomic Collisions*, American Institute of Physics Press, New York, 1993, pp. 350–359, and references therein.
- [18] P. Duffy, *Can. J. Phys.* 74 (1996) 763.
- [19] L.J. Sham, *Phys. Rev. B* 32 (1985) 3876.
- [20] M.E. Casida, *Phys. Rev. A* 51 (1995) 2505.
- [21] M.E. Casida, *Phys. Rev. B* 59 (1999) 4694.
- [22] P.R. Koren, F. Chen, E.R. Davidson, *Mol. Phys.* 99 (2001) 1329.
- [23] C. Filippi, C.J. Umrigar, C.J. Taut, *J. Chem. Phys.* 100 (1944) 1290.
- [24] C.J. Umrigar, X. Gonze, *Phys. Rev. A* 50 (1994) 3829.
- [25] Q. Zhao, R.C. Morrison, R.G. Parr, *Phys. Rev. A* 50 (1994) 2138.
- [26] R.T. Sharp, G.K. Horton, *Phys. Rev.* 90 (1953) 317.
- [27] J.C. Slater, *Phys. Rev.* 81 (1951) 385.
- [28] S. Hamel, M.E. Casida, D.R. Salahub, *J. Chem. Phys.*, submitted for publication.
- [29] J.D. Talman, W.F. Shadwick, *Phys. Rev. A* 14 (1976) 36.
- [30] J.B. Krieger, Y. Li, G.J. Iafrate, *Int. J. Quant. Chem.* 41 (1992) 489.
- [31] J.D. Talman, *Comp. Phys. Commun.* 54 (1989) 85.
- [32] L.J. Sham, M. Schlüter, *Phys. Rev. Lett.* 51 (1983) 1888.
- [33] J.B. Krieger, Y. Li, G.J. Iafrate, in: E.K.U. Gross, R.M. Dreizler (Eds.), *Density Functional Theory*, Plenum Press, New York, 1995, p. 191.
- [34] T. Grabo, T. Kreibich, S. Kurth, E.K.U. Gross, in: V.I. Anisimov (Ed.), *Strong Coulomb Correlations in Electronic Structure Calculations: Beyond the Local Density Approximation*, Gordon and Breach, 1999, pp. 203–311.
- [G99] A. Görling, *Phys. Rev. Lett.* 83 (1999) 5459.
- [IHB99] S. Ivanov, S. Hirato, R.J. Bartlett, *Phys. Rev. Lett.* 83 (1999) 5455.

- [37] M.E. Casida, C. Jamorski, J. Guan, S. Hamel, D.R. Salahub, *DEMON-DYNARHO* version 3.1, deMon Software, 2001.
- [38] (a) A. St-Amant, D.R. Salahub, *Chem. Phys. Lett.* 169 (1990) 387;  
(b) A. St-Amant, Ph.D. Thesis, University of Montreal, Montreal, 1992;  
(c) M.E. Casida, C. Daul, A. Goursot, A. Koester, L.G.M. Pettersson, E. Proynov, A. St-Amant, D.R. Salahub principal authors, H. Duarte, N. Godbout, J. Guan, C. Jamorski, M. Leboeuf, V. Malkin, O. Malkina, M. Nyberg, L. Pedocchi, F. Sim, L. Triguero, A. Vela contributing authors, *DEMON-KS* version 4.0, deMon Software, 1997.
- [39] A.O. Bawagan, Ph.D. Thesis, University of British Columbia, Vancouver, 1987.
- [40] S. Hamel, M.E. Casida, D.R. Salahub, *J. Chem. Phys.* 114 (2001) 7342.
- [41] A.J. Sadlej, *Coll. Czech. Chem. Commun.* 53 (1988) 1995; A. Sadlej, *Theor. Chim. Acta* 79 (1991) 123.
- [D89] T.H. Dunning Jr., *J. Chem. Phys.* 90 (1989) 1007.
- [KDH92] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, *J. Chem. Phys.* 96 (1992) 6796.
- [44] K.P. Huber, G. Herzberg, *Constants of Diatomic Molecules*, Van Nostrand-Reinhold, New York, 1979.
- [45] K.-H. Hellwege, A.M. Hellwege (Eds.), *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, Structure Data of Free Polyatomic Molecules*, Vol. 7, Springer-Verlag, New York, 1976.
- [KLI90] J.B. Krieger, Y. Li, G.J. Iafrate, *Phys. Lett. A* 148 (1990) 470.
- [47] P. Duffy, D.P. Chong, *Org. Mass Spectrosc.* 28 (1993) 321.
- [48] C.-H. Hu, D.P. Chong, *J. Chin. Chem. Soc.* 47 (2000) 141.
- [BA80] G. Bieri, L. Åsbrink, *J. Electron. Spectrosc. Rel. Phenom.* 20 (1980) 149.
- [50] P. Duffy, S.A.C. Clark, C.E. Brion, M.E. Casida, D.P. Chong, E.R. Davidson, C. Maxwell, *Chem. Phys.* 165 (1992) 183.
- [51] C.-H. Hu, D.P. Chong, M.E. Casida, *J. Electron Spectr.* 85 (1997) 29.
- [52] Y. Shigeta, A.M. Ferreira, V.G. Zakrzewski, J.V. Ortiz, *Int. J. Quantum Chem.*, in press.
- [53] J. Garza, J.A. Nichols, D.A. Dixon, *J. Chem. Phys.* 113 (2000) 6029.
- [CS00] M.E. Casida, D.R. Salahub, *J. Chem. Phys.* 113 (2000) 8918.
- [B88] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [P86] J.P. Perdew, *Phys. Rev. B* 33 (1986) 8822.
- [57] M.M. Pant, J.D. Talman, *Phys. Rev. A* 17 (1978) 1819.
- [58] M.E. Casida, D. P Cong, *Chem. Phys.* 133 (1989) 47; erratum *Chem. Phys.* 136 (1989) 489.
- [59] Y. Zheng, J.J. Neville, C.E. Brion, *Science* 270 (1995) 786.
- [60] J.P. Perdew, M.R. Norman, *Phys. Rev. B* 26 (1982) 1884.
- [61] R.W. Godby, M. Schlüter, L.J. Sham, *Phys. Rev. B* 36 (1987) 6497.
- [62] P. Politzer, F. Abu-Awwad, *Theor. Chem. Acc.* 99 (1998) 83.