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Photoelectron angular distributions beyond the dipole approximation: a computational study on the N_2 molecule

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Abstract

Contributions of the first-order nondipole terms to the photoelectron angular distributions from randomly oriented nitrogen molecules have been calculated in the framework of density functional theory and by employing a single centre expansion for the bound and continuum wavefunctions. Both valence and inner-shell ionizations have been considered in a photon energy range from threshold up to 2000 eV. Our results agree reasonably with calculations based on the random phase approximation and with the experimental data available. Our results for core ionizations confirm the most recent experimental finding of rather small nondipole effects in the near-threshold range. However, nondipole terms turn out to be quite large, even at the threshold, when individual contributions from the $1\sigma_g^{-1}$ and $1\sigma_u^{-1}$ ionization channels are considered. Strong interference effects leading to high-energy oscillations in the dipole and nondipole asymmetry parameters are satisfactorily explained within the Cohen–Fano model.

1. Introduction

Studies of low-energy photoionization dynamics usually base their analysis of angle resolved photoionization intensities on the dipole approximation (DA) to the photon–electron interaction. In the DA the differential cross section of photoelectrons assumes a particularly simple functional form, since only two independent dynamical parameters are required:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{\sigma}{4\pi} [1 + (-1/2)^{|m_r|} \beta P_2(\cos\theta)]. \tag{1}$$

In equation (1) Ω denotes the direction of the photoelectron momentum vector, \vec{k}, σ is the angle integrated cross section and β is the dipolar angular asymmetry parameter; m_r specifies

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the polarization of the photon beam. $m_r = 0$ for linearly polarized light, whose electric vector $\hat{\epsilon}$ then defines the \hat{Z} axis of the laboratory frame (LF). $m_r = \pm 1$ for left (+1) and right (-1) circularly polarized light propagating along the polar LF axis.

Experimental evidences of the breakdown of the DA already in the VUV region of the spectrum have been provided from the photoionization of rare-gas atoms, such as Ne [1] and Xe [2] where departures from the dipolar behaviour are observed for photon energies as low as few tens of eV (see [3, 4] for recent reviews). While for atoms, the experimental findings have been successfully explained by theoretical calculations based either on the independent particle picture [5, 6] or the random phase approximation (RPA) [2, 7], experimental and theoretical works in molecules have been very limited so far. Notably, two papers focusing on the K-shell photoionization of molecular nitrogen report contradicting experimental results [8–10]. While the first measurements gave evidence of strong nondipole effects at very low photoelectron kinetic energies [8, 9], results of a recent investigation strongly contradict earlier findings [10]. In the work of [10] negligible nondipole effects are detected, even if strong near-threshold departures from the dipolar behaviour are theoretically predicted for the individual $1\sigma_g^{-1}$ and $1\sigma_u^{-1}$ ionization channels [10].

With the aim to resolve this controversy, we decided to calculate nondipolar contributions to the angular distributions of photoelectrons from molecular nitrogen. Calculations are reported in a photon energy range from threshold up to 2000 eV (an energy interval where first-order corrections to the DA should prove adequate [5, 6]) and for each main-line orbital ionization. The nitrogen molecule has been further selected because it is a quite well-studied system for which experimental data exist both for the outer-valence and K-shell ionizations: comparison with experiments allows us for a sound evaluation of the accuracy of the theoretical method proposed. The nitrogen molecule is also the natural candidate for further experimental studies and we believe that accurate theoretical data, though at the independent electron approximation, would prove useful for stimulating new experimental efforts.

The organization of the paper is as follows. In section 2 we will briefly outline our theoretical approach and the computational details. In section 3 we will discuss our results, and a comparison with previous investigations will be made. Our conclusions and perspectives are then summarized in the final section.

2. Theoretical and computational details

Under conditions at which the first-order corrections to the DA suffice (photon energies below several keV) corrections to the DA arising from electric-dipole–electric-quadrupole (E1–E2) and electric-dipole–magnetic-dipole (E1–M1) interference terms are accounted through the introduction of two independent angular distribution dynamical parameters, γ and δ [5, 6]:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos\theta) + (\delta + \gamma \cos^2\theta)\sin\theta\cos\phi]$$
(2)

for pure linearly polarized light along the LF \hat{Z} axis, and

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{\sigma}{4\pi} [1 - \beta/2P_2(\cos\theta) + (\gamma/2\sin^2\theta + \delta)\cos\theta]$$
(3)

for circularly polarized light propagating along the LF \hat{Z} axis. Here θ and ϕ denote the polar angles of the photoelectron momentum vector \vec{k} in the LF, the positive \hat{X} axis being defined by the photon propagation vector for linearly polarized light.

Nondipolar effects manifest themselves through backward/forward anisotropies along the photon momentum. These can be forward directed, for positive values of γ and δ , or backward for negative values of the parameters.

In our computer codes the photoelectron wavefunction $\psi_{\vec{k}}^{(-)}$ satisfying 'incoming-wave' boundary conditions is defined as (atomic units are used throughout the paper)

$$\psi_{\vec{k}}^{(-)} = \sum_{p\mu hl} \mathbf{i}^{l} \, \mathbf{e}^{-\mathbf{i}\sigma_{l}} X_{lh}^{p\mu*}(\Omega) \psi_{lh}^{p\mu(-)} \tag{4}$$

for any positive $E = \frac{\vec{k}^2}{2}$ photoelectron kinetic energy. In equation (4) σ_l is the Coulomb phaseshift of the *l*th partial wave and $\psi_{lh}^{p\mu(-)}(\vec{r})$ are the set of *S*-matrix normalized eigenchannels functions [11, 12]. $X_{lh}^{p\mu}$ is a symmetry-adapted angular basis function for the *ps* irreducible representation (IR) of the molecular point group [12], $X_{lh}^{p\mu} = \sum_m b_{lmh}^{p\mu} Y_{lm}(\theta, \phi)$ with the $b_{lmh}^{p\mu}$ sets of coefficients defining the unitary transformation between spherical harmonics and the symmetry adapted basis set. The dipolar asymmetry parameter β is then defined as usual:

$$\beta = \frac{\sqrt{30}}{\sum_{p\mu lh\lambda_r} \left| D_{lh}^{p\mu(-)}(\lambda_r) \right|^2} \sum_{\substack{p\mu lhm\lambda_r\\p'\mu'l'h'm'\lambda'_r}} i^{(l'-l)} e^{i(\sigma_l - \sigma_{l'})} b_{hlm}^{p\mu} b_{h'l'm'}^{p'\mu'*} D_{lh}^{p\mu(-)}(\lambda_r) D_{l'h'}^{p'\mu'(-)*}(\lambda'_r) \times (-)^{m+\lambda_r} \sqrt{(2l+1)(2l'+1)} \begin{pmatrix} l & l' & 2\\ -m & m' & \varepsilon \end{pmatrix} \begin{pmatrix} l & l' & 2\\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & 2\\ \lambda_r & -\lambda'_r & -\varepsilon \end{pmatrix},$$
(5)

while nondipole parameters δ and γ of equations (2) and (3) are expressed through the values

$$A_{L}^{E1\cdot M1}(k) = \sum_{\substack{p \neq l h m \lambda_r \\ p' \mu' l' h' m' \lambda'_r}} i^{(l'-l)} e^{i(\sigma_l - \sigma_{l'})} b_{hlm}^{p\mu} b_{h'l'm'}^{p'\mu'*} D_{lh}^{p\mu(-)}(\lambda_r) M_{l'h'}^{p'\mu'(-)*}(\lambda'_r) \times (-)^{m+\lambda_r} \sqrt{(2l+1)(2l'+1)} \begin{pmatrix} l & l' & L \\ -m & m' & \varepsilon \end{pmatrix} \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & L \\ \lambda_r & -\lambda'_r & -\varepsilon \end{pmatrix}$$
(6)

and

$$A_{L}^{E1\cdot E2}(k) = \sum_{\substack{p \neq l h m \lambda_r \\ p' \mu' l' h' m' \lambda'_r}} i^{(l'-l)} e^{i(\sigma_l - \sigma_{l'})} b_{hlm}^{p\mu} b_{h'l'm'}^{p' \mu'*} D_{lh}^{p\mu(-)}(\lambda_r) Q_{l'h'}^{p' \mu'(-)*}(\lambda'_r) \times (-)^{m+\lambda_r} \sqrt{(2l+1)(2l'+1)} \begin{pmatrix} l & l' & L \\ -m & m' & \varepsilon \end{pmatrix} \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 2 & L \\ \lambda_r & -\lambda'_r & -\varepsilon \end{pmatrix}.$$
(7)

Properties of the Wigner 3*j* symbols restrict *L* to L = 0, 1, 2 and L = 1, 2, 3 in equations (6) and (7), respectively. Also the L = 0 term is not present if linearly polarized light is used and even-*L* quantities further vanish for achiral molecules in the same way as odd L = 1 multipole vanishes in the DA [13, 14]. The dynamical quantities $D_{lh}^{p\mu(-)}(\lambda_r), M_{lh}^{p\mu(-)}(\lambda_r)$ and $Q_{lh}^{p\mu(-)}(\lambda_r)$ in equations (5)–(7) are electric/magnetic-dipole and electric-quadrupole matrix elements between final continuum and bound initial states, respectively, i.e.,

$$D_{lh}^{p\mu(-)}(\lambda_r) = \sqrt{\frac{4\pi}{3}} \langle \psi_{lh}^{p\mu(-)} | r Y_{1\lambda_r} | \varphi_i \rangle.$$
(8a)

$$M_{lh}^{p\mu(-)}(\lambda_r) = \left\langle \psi_{lh}^{p\mu(-)} \middle| L_{\lambda_r} | \varphi_i \rangle.$$
(8b)

$$Q_{lh}^{p\mu(-)}(\lambda_r) = \sqrt{\frac{4\pi}{5}} \langle \psi_{lh}^{p\mu(-)} | r^2 Y_{2\lambda_r} | \varphi_i \rangle.$$
(8c)

 L_{λ_r} being the λ_r -spherical component of the electronic angular momentum (the orbital part only in a non-relativistic treatment as it is done here). Then γ and δ can be expressed as

$$\gamma = -\frac{\sqrt{15 \times 7}}{\sum_{p\mu lh\lambda_r} \left| D_{lh}^{p\mu(-)}(\lambda_r) \right|^2} \omega \alpha \operatorname{Im} \left(A_3^{E1 \cdot E2} \right)$$
(9)

and

$$\delta = \frac{3\alpha}{\sum_{p\mu lh\lambda_r} \left| D_{lh}^{p\mu(-)}(\lambda_r) \right|^2} \left[\sqrt{\frac{3}{2}} \operatorname{Im}(A_1^{E1 \cdot M1}) + \omega \sqrt{\frac{3}{10}} \operatorname{Im}(A_1^{E1 \cdot E2}) + \omega \sqrt{\frac{7}{15}} \operatorname{Im}(A_3^{E1 \cdot E2}) \right],$$
(10)

where α is the fine-structure constant whereas Im in equations (9), (10) means the imaginary part of the argument has to be taken. Chirality of the molecular system further introduces additional parameters, expressed through the quantities defined in equations (6), (7) but involving even multipoles [14]. Note further from equations (9), (10) that the electricquadrupole interference terms increase linearly with photon energy, whereas the only photonenergy dependence of the magnetic-dipole interference terms is contained in the dipole matrix element; E1–E2 interference terms cannot be neglected for high photon energies.

Photoelectron angular distributions for each orbital ionization of the nitrogen molecule have been calculated with our single centre expansion (SCE) approach based on a density functional Kohn–Sham (KS) Hamiltonian [15], DFT–SCE, modified for the calculation of the first-order nondipolar asymmetry parameters. The Hamiltonian is represented on the SCE basis set which is taken as a product of a radial B-spline function [16] of a given order (ten in the present calculation) and a symmetry-adapted spherical harmonic:

$$\chi_{nlh}^{p\mu,\text{SCE}} = \frac{1}{r} B_n(r) X_{lh}^{p\mu}(\theta,\phi).$$
(11)

Bound state solutions are obtained with a generalized diagonalization of the KS Hamiltonian matrix, constructed given the ground-state density. The ground-state density of N₂ is obtained by a conventional bound state calculation at the equilibrium distance of 2.068 au employing the ADF molecular code [17, 18] with a double- ζ plus polarization basis set (DZP) of Slater-type orbitals. The LB94 exchange-correlation (*xc*) potential [19] is employed because it ensures the correct asymptotic behaviour. Scattering solutions are extracted as the set of linearly independent eigenvectors of the energy-dependent matrix $A^{\dagger}A$, i.e. $A^{\dagger}A(E)c = ac$ corresponding to minimum modulus eigenvalues *a* with A(E) = H - ES, *H* and *S* being the Hamiltonian and overlap matrices over the SCE basis set, respectively [20].

The highest angular momentum employed (l_{max}) is 80 for expanding the bound and continuum orbitals with the origin of the SCE placed at the centre of mass of the molecule. Two different basis sets are used for the photon energy range (up to 2000 eV) investigated. In the near-threshold and intermediate energy range (up to 300 eV of photoelectron kinetic energy, KE), the *B*-splines are built over a linear radial grid extending up to 20.0 au with a step size of 0.20 au, whereas a linear grid with a finer mesh (0.10 au) extending up to 15.0 au is used for higher excitation energies. For computational convenience the radial basis set is properly truncated [21] in such a way that only partial waves with $l \leq 11$ and $l \leq 25$ contribute to the expansion of the continuum wavefunction in the two energy regions respectively. The convergence of the partial wave expansions has been tested in preliminary calculations. Photoelectron kinetic energies are converted to photon energies by using the experimental ionization potential (IP) values [22–24].



Figure 1. Single-channel DFT–SCE angular distribution parameters for the $3\sigma_g^{-1}$ orbital ionization of the N₂ molecule. Also reported are the experimental β values from [25, 26] and RPA results from [28]. The experimental and the theoretical FCHF data sets for ζ are taken from [27].

3. Results and discussion

Both dipole and nondipole DFT-SCE angular distribution parameters for the $3\sigma_g^{-1}$ orbital ionization are plotted in figure 1, together with the experimental data available from the literature [25–27] and the RPA results of Cacelli *et al* [28] for the dipole asymmetry parameter. The partial cross section is characterized by a well-studied low-energy $\varepsilon \sigma^*$ shape resonance [29] whose signature is a strong near-threshold modulation in the β asymmetry parameter. Our results for β agree reasonably with the experimental data [25, 26] and with both the single channel and RPA calculations of Cacelli et al [28] (only the RPA results of [28], in the length and velocity gauges of the interaction operator, are reported in the figure); the discrepancies between our results and the RPAs below 20 eV of photon energy being due to the lack of inter channel coupling in our treatment. Nondipole parameters are sensitive to the shape-resonant dynamics because a strong oscillation characterizes their near-threshold behaviour. The different magnitudes of the two parameters γ and δ are worth noting; the former is roughly more than an order of magnitude bigger than the latter, a well-documented characteristic found in the photoionization from atoms and which is also observed in the scattering from a multicentric potential. The contribution of δ to the ζ parameter, $\zeta = \gamma + 3\delta$, (which is the actual measured quantity for some experimental setups [9]) is, however, not negligible and its correct evaluation is needed when a quantitative agreement with the experimental data is sought. The most intriguing phenomenon shows up for higher photon energies, away from threshold, where nondipole corrections become of comparable magnitude to β . In fact,



Figure 2. Single-channel DFT–SCE angular distribution parameters for the $1\pi_u^{-1}$ orbital ionization of the N₂ molecule. Also reported are the experimental β values from [25, 26] and RPA results from [28].

strong high-energy oscillations superimposed on a rising background, beginning just beyond the shape-resonance region and persisting up to the highest photon energy explored, are seen in both the dipole and nondipole asymmetry parameters. These modulations show up rather damped in the dipole parameter, but are seen to acquire amplitude in the nondipole terms as the excitation energy increases. These oscillations take their origin from the bicentric nature of the electron-ion interaction, and have been discussed since long ago by Cohen and Fano [30] in the photoionization from H⁺₂. Resorting to a Born approximation calculation and a partialwave analysis, the authors showed that modulations in the photoionization cross sections could be related to the onset of partial wave channels of increasing *l*; the higher the excitation energy, the easier the photoelectron can overcome the centrifugal barrier characteristic of continuum states with high l values. Then modulations are predicted to superimpose on the slowly varying background due to the $[1 + (\sin kR)/kR]$ term, R being the equilibrium bond length [30]. The model will be used later, when studying the N 1s photoionization, for obtaining an estimate of the nitrogen bond length. Note that oscillations in the γ and δ parameters occur almost out of phase. Scattering dynamics enter differently in the definition of the various asymmetry parameters, creating a phase difference in their energy-dependent behaviour. Finally, the good agreement found between the present results for the ζ parameter and the experimental and theoretical data available from the literature [27] are worth noting.

We next consider the photoionization from the $1\pi_u$ orbital, the corresponding DFT–SCE angular distribution parameters being plotted in figure 2. The experimental values [25, 26]



Figure 3. Single-channel DFT–SCE angular distribution parameters for the $2\sigma_u^{-1}$ orbital ionization of the N₂ molecule. Also reported are the experimental β values from [25, 26] and RPA results from [28].

and the RPA results of Cacelli *et al* [28] for the dipole asymmetry parameter are also reported. In rather good agreement with the RPA predictions [28] the KS β parameter starts with a value close to zero just above the opening of the photoionization channels and reaches a maximum value below 100 eV of photon energy; the β profile then slowly decreases with damped modulations for higher excitation energies. The nondipole parameters γ and δ do not show interesting features in the near-threshold region; a sudden increase from values close to zero is followed by oscillating patterns of increasing amplitudes, similar to the $3\sigma_g^{-1}$ ionization. The high-energy behaviour of the δ parameter is characterized by fairly large values, leading thus to sizeable differences between ζ and γ values. The complex multicentric scattering dynamics is also responsible for a phase difference in the γ s and δ s oscillations.

A markedly different situation is encountered when examining the DFT–SCE angular distribution parameters for the remaining valence levels of the N₂ molecule, which are plotted in figures 3 and 4 for the $2\sigma_u^{-1}$ and $2\sigma_g^{-1}$ ionizations, respectively, together with the experimental values [25, 26] and the RPA results of Cacelli *et al* [28] for β . The nondipole parameters δ and γ behave quite similarly for these two ionizations in the high-energy interval; in particular δ assumes negligible absolute values in either case, contributing to the corresponding ζ in a limited extent only. The near-threshold behaviour of the angular distribution parameters is strongly dependent on the particular orbital ionization, however. We are not dealing ourselves with details on their specific behaviour, since a KS treatment of the photoeffect is known to



Figure 4. Single-channel DFT–SCE angular distribution parameters for the $2\sigma_g^{-1}$ orbital ionization of the N₂ molecule. Also reported are the experimental β values from [26] and RPA results from [28].

overestimate the $2\sigma_g^{-1}$ cross section just above threshold compared to the experiment [31] and electron-correlation effects, completely neglected in a KS treatment, are also expected to affect the near-threshold scattering dynamics following the $2\sigma_u^{-1}$ ionization [31, 32], so that the predictive power of the theory is limited in this case.

We finally consider the K-shell ionization, for which experimental and theoretical calculations from different sources are available [8–10]. There have been two independent measurements of nondipolar angular distributions, giving contradicting conclusions. The experimental work by Hemmers *et al* [9] revealed a resonant behaviour in the ζ parameter with a peak energy position of about 60 eV above threshold. The peak energy position of the feature in the ζ profile is, therefore, difficult to correlate with the well-known σ^* shape-resonance in the $1\sigma_g^{-1}$ cross section [33]. Recent measurements [10] do not support these findings, however, and negligible deviations from the dipole distributions in the near-threshold region are found. We report our DFT–SCE results in figure 5, and make a comparison with the experimental β measurements [8, 10, 34] and the two sets of experimental data for the nondipole parameters [9, 10]. We report DFT–SCE results resolved in the corresponding partial cross sections. Our results are fully consistent with the experimental results of [10]; DFT–SCE results for the γ parameter are in a very good agreement with the experimental uncertainties.



Figure 5. Single-channel DFT–SCE angular distribution parameters for the $1\sigma_g^{-1}$ and $1\sigma_u^{-1}$ orbital ionizations from the N₂ molecule as well as their average, weighted by the corresponding cross section. Also included are the experimental β data taken from [8, 10, 34]. The experimental values for the nondipole parameters are taken from Hemmers *et al* [9] and Hosaka *et al* [10].

Strong near-threshold deviations from the DA are predicted for the individual $1\sigma_g^{-1}$ and $1\sigma_u^{-1}$ ionization channels, in nice agreement with the RPA results of [10], but almost a complete cancellation occurs in the average values which display smooth and monotonic variations in the whole spectral range, resembling the atomic case [9]. This is a nice example of a coherent electron emission from two identical sites, whose quantum coherence is obscured with experiments that do not resolve the individual quantum (gerade and ungerade) states [35]. Our DFT–SCE results are in rather good agreement with the RPA predictions of [10] (not reported in the figure for the sake of clarity), with the only exceptions of a near-threshold oscillation in the δ parameter which is absent in our results, and a small shift of the RPA γ profiles for the individual $1\sigma_g^{-1}$ and $1\sigma_u^{-1}$ ionization channels towards higher excitation energies when compared to our results, due to a different attractive character in the effective KS and RPA scattering potentials. The statement that nondipole effects prove negligible for nitrogen K-shell photoionization in the near-threshold range is, therefore, put on a firm basis because results from two different theoretical approaches are in a satisfactory agreement with each other and with the new experimental data of Hosaka et al [10]. The extent of the agreement between our theoretical results and the RPAs of [10] furthermore suggests that inter-channel coupling effects between main-line $1\sigma_g^{-1}$ and $1\sigma_u^{-1}$ ionization channels prove

quite unimportant in determining deviations from the dipolar angular distribution and further that relaxation effects are phenomenologically rather well accounted for by the LB94 xc potential [36].

We now analyse the high-energy behaviour of the various asymmetry parameters. The individual $1\sigma_g^{-1}$ and $1\sigma_u^{-1}$ asymmetry parameters are seen to oscillate out-of-phase; the oscillations are characterized by a rather small amplitude in the β parameter but they persist without damping in the γ and δ profiles. The out-of-phase oscillations originate from the different parities of the initial states, and consequently, of the continuum partial waves, and this, as stressed above, leads to cancellations in the averaged values. This strong oscillatory character furnishes a nice proof of the validity of the Cohen–Fano model, which is then invoked for its explanation. In fact, consider in figure 5 the crossing points of the γ parameters for the $1\sigma_g^{-1}$ and $1\sigma_u^{-1}$ states: they occur approximately in steps of 1.5 au of photelectron momentum. Then, assuming a sin(kR) dependence as implied by the Cohen–Fano model [30] we arrive at a distance R of 2.09 au in nice agreement with the equilibrium distance of 2.07 au used as input in our fixed-nuclei calculations, and with the results of a similar analysis presented by Hosaka *et al* [10].

4. Conclusions

Deviations of the photoelectron angular distributions from the DA have been calculated for randomly oriented nitrogen molecules, by using a DFT approach and a single centre expansion for the bound and continuum wavefunctions. Our DFT-SCE results agree reasonably well with recent RPA calculations and with the available experimental data in the nearthreshold range. For core ionizations our results are fully consistent with the most recent theoretical and experimental findings [10] and rather small nondipole effects are found in the near-threshold range. However nondipole terms turn out to be quite large, even at the threshold, when individual contributions from the $1\sigma_g^{-1}$ and $1\sigma_u^{-1}$ ionization channels are considered. Interference effects giving rise to high-energy oscillations in the dipole and nondipole asymmetry parameters, and which are found for both valence and core ionizations, are analysed and explained in the framework of the Cohen-Fano model. The DFT-SCE approach appears a reliable tool for studying nondipolar effects in molecular photoelectron angular distributions: results obtained are of comparable accuracy of available data from RPA approaches. Efforts are currently made towards the inclusion of a multicentric basis set [37] which would permit the study of more extended systems and chiral molecules. Also inclusion of dynamical correlation effects in the framework of the linear response theory is underway.

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