

## K-edge circular dichroism of amino acids: Comparison of random phase approximation with other methods

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Soft X-ray natural circular dichroism (CD) of amino acids is studied by means of *ab initio* methods. Several approaches to evaluate the oscillator and rotary strengths of core-to-valence excitations are compared from the viewpoint of basis set dependence. It was shown that, among considered methods, the random phase approximation (RPA) provides most consistent and less time-consuming results for CD core excitation spectra. Discussion of the low energy part of K-edge CD spectra of five common amino acids (alanine, serine, phenylalanine, asparagine, and lysine) obtained with the help of RPA is presented<sup>1</sup>.

Chiral centers are rather common in biological systems. For example, chiral amino acids appear in constituents of proteins in the living matter. Near edge X-ray absorption spectroscopy (XAS) is a powerful tool for studying of bio molecules: according to the "building block principle" it is possible to correlate specific XAS features with functional groups or with individual bond. Moreover, clear fingerprints of bio-molecules may be obtained using soft X-ray natural circular dichroism (XNCD) spectra: particular functional groups with similar XAS may have different chiral properties. The XNCD shows a very tiny effect. The normalized difference in absorption of the left and right components of the light  $g=2(I_L-I_R)/(I_L+I_R)\approx 10^{-3}$  on the core-to-valence transitions, which makes the observation of that effect rather difficult. Very few experimental and theoretical studies of XNCD in amino acids are available<sup>2,3</sup>.

In the present paper we evaluate the RPA approach, which allows to predict the XNCD on low-lying transitions for rather big molecules with relatively small computational efforts. We compare different approaches to describe the excited orbitals in application to XNCD properties of amino acids: ground state Hartree-Fock (HF) orbital set employed in (i) RPA and (ii) static exchange approach (STEX) (unrelaxed), (iii) core-ionized state HF orbital set applied in STEX(relaxed) and (iv) HF excited state orbital set for each core-to-valence excited state. Furthermore in (i) the DFT-RPA method is compared with the RPA where the *ab initio* HF orbital set is used. In (iv), the oscillator and rotary strengths evaluated by different orbital sets for the initial and final states, namely, non-orthogonal ground-state and core-excited HF orbitals, are compared with those evaluated by using the core-excited HF orbital set

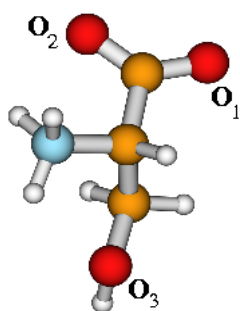


Figure 1. L-serine

to describe the initial (ground) state. Oscillator  $f_{ge}$  and rotary  $R_{ge}$  strength on the core-to-valence transitions can be computed in two alternative ways using electric dipole momentum integrals between ground  $g$  and core-excited  $e$  states in length ( $L$ ) and velocity ( $V$ ) forms. We used the smallness of the relative difference of oscillator strength  $\Delta_f=2|f_{ge}^L-f_{ge}^V|/(f_{ge}^L+f_{ge}^V)$  and the angle between electric dipole transition vectors in length and velocity forms  $\beta_{ge}$  as a check for basis set completeness and results consistency. Calculations of L-serine (Fig.1) O<sub>1</sub> K-edge using different methods are presented in Table 1 and Figure 2. The energy position of the

excited states  $\omega_{ge}$  in RPA and STEX (unrelaxed) are overestimated comparing to STEX(relaxed) and HF calculations. RPA, which takes into account some correlation effects and some orbital reorganization effects, improving excited orbital character in the core-excited states, shows the best consistence among considered methods (smallest  $\Delta_f$  and  $\beta_{ge}$ ). The electron correlation effect is important for proper description of the core-to-valence excitation. Use of non-orthogonal basis set for the HF excited state calculation decreases  $\Delta_f$  sufficiently, and shifts the values of oscillator strength toward the RPA and STEX(unrelaxed) results.

The basis set dependence of the XNCD spectra for different approaches is studied systematically for different methods using variation of Woon and Dunning basis sets up to aug-cc-pCV5Z. The RPA calculation shows most satisfactory and self-consistent results for the low-lying core-to-valence excitations near the O K-edge. A

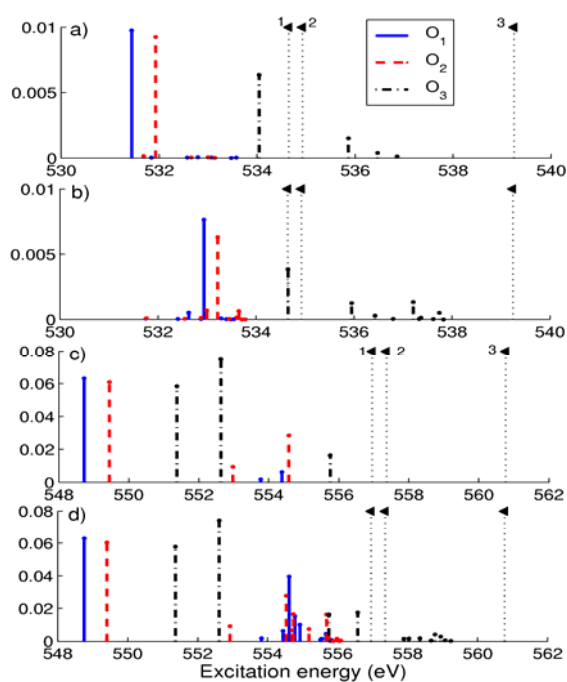


Figure 2. Oscillator strength for L-serine O K-edge: a) HF (orth); b) STEX(rel); c) STEX (unrel); d) RPA.

clear convergence of the oscillator strength for the basis sets larger than triple-zeta was found for the RPA approach. Use of extended quadrupole-zeta or larger basis sets are required to obtain satisfactory results for the rotary strength on the O K-edge. Using the RPA approach the calculation of the oscillator, rotary strength and asymmetry factor on the oxygen, nitrogen and carbon K-edge were performed for L-isomers of five common amino acids<sup>1</sup>. In spite of rather poor definition of excitation energies by using the ground state HF orbital set, the RPA approach provides quite satisfactory results for relative intensities of absorption and XNCD spectral lines. The relative simplicity of the RPA technique using the same ground-state HF orbital set for any core-to-valence excitation makes it applicable to chiral centers in rather big compounds, like proteins.

Table 1. L-serine O<sub>1</sub> K-edge

	$\omega_{ge}(\text{eV})$	$f_{ge}^l$	$\Delta_f$	$\beta_{ge}$	$R_{ge}^l$	$R_{ge}^v$	$g_{ge}(10^{-5})$
<b>STEX(rel)</b>	532.94	0.0077	0.34	0.02	210.4	3.01	2558
<b>STEX(unrel)</b>	548.73	0.0632	0.07	0.003	169.7	-4.33	296
<b>RPA</b>	548.76	0.0628	0.03	0.0001	1.99	-1.68	3.64
<b>HF(orth)</b>	531.44	0.0098	0.38	0.01	144.4	0.82	1346
<b>HF(non-orth)</b>	531.44	0.0560	0.11	0.006	321.6	4.09	598

<sup>1</sup> V. Kimberg and N.Kosugi, J Chem. Phys **126**, 245101 (2007)

<sup>2</sup> M. Tanaka, K. Nakagawa, A. Agui, K. Fujii, and A. Yokoya, Physica Scripta, **T115**, 873 (2005) (experiment)

<sup>3</sup> O. Plashkevych, V. Carravetta, O. Vahtras and H. Ågren, Chem. Phys. **232**, 49 (1998) (theory)