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Erratum: "Multi-reference approach to the calculation of photoelectron spectra including spin-orbit coupling" [J. Chem. Phys. 143, 074104 (2015)]

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In Ref. 1 we have presented a novel first principles approach to the calculation of photoelectron spectra (PES) and a comparison with the widely used sudden approximation (SA)[2–4] has been performed. Two mistakes have been made in Ref. 1 which are corrected in this erratum. First, within the SA the intensity of a transition is proportional to the absolute square of the Dyson orbital (DO) norm

$$\sigma(\mathcal{E}_k) \propto \left|\left\langle \Psi_F^{N-1} \middle| \hat{a} \Psi_I^N \right\rangle\right|^2. \tag{1}$$

However, in Figs. 2 and 5 of Ref. 1, the DO norm was not squared. Second, Eq. (10) from the original publication contained a typo and should read

$$\left|D_{FI}^{\text{SA}}\right|^2 = \left|\left\langle \Psi_F^{N-1} \psi^{\text{el}}(\mathbf{k}) \middle| \hat{\mathbf{d}} \middle| \Psi_I^N \right\rangle\right|^2 \approx \left|\left\langle \Psi_F^{N-1} \middle| \hat{a} \Psi_I^N \right\rangle\right|^2. \tag{2}$$

Taking the square alters the discussion on the applicability of the SA to the calculation of X-ray PES of transition metal compounds. We emphasize that the main results of Ref. 1, i.e., the PES obtained via the numerical integration of the DO with the ionized electron wave function, are not affected.

The corrected SA PES are presented in Fig. 1 together with the full calculation results. In contrast to what is claimed in Ref. 1, Fig. 1 shows that the SA predicts the intensities of all peaks with an accuracy that is comparable to the full calculation.
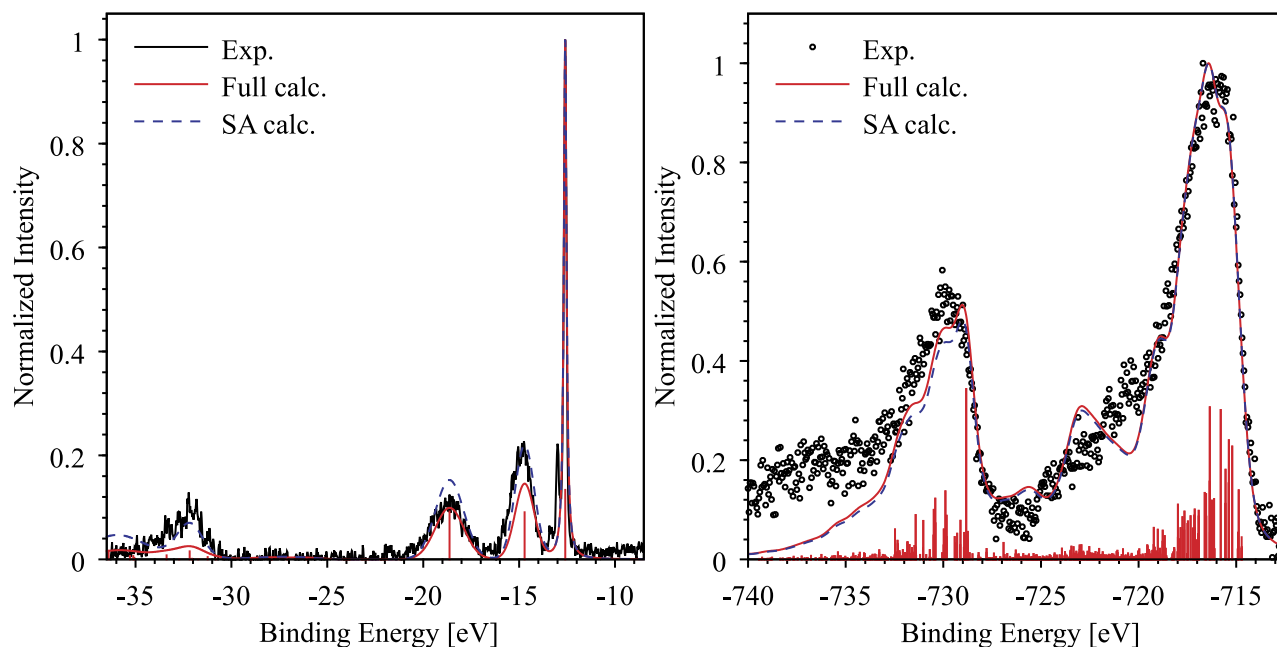

FIG. 1. (Left panel) Calculated and experimental PES of the gas-phase water for 180 eV photon energy. (Right panel) Experimental (2M FeCl$_2$ aqueous solution) and calculated (for the [Fe(H$_2$O)$_6$]$^{2+}$ cluster) core PES for 925 eV photon energy.

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Thus, the SA provides a good approximation to the full calculation of L-edge core PES of $[Fe(H_2O)_6]^{2+}$ where the kinetic energy of the outgoing electron is quite high and all transitions have the same character, i.e., being ionizations from the 2p orbitals.

Although the results obtained within the SA for the L-edge PES of $[Fe(H_2O)_6]^{2+}$ are quite accurate, the SA should be used with caution. If the spectrum contains transitions involving DOs of different character, e.g., localized on metal and ligands, or the kinetic energy of the outgoing electron is low, the applicability of the SA should be investigated on a case to case basis. We would like to stress that the protocol proposed in Ref. 1 that utilizes the numerical integration for the matrix elements allows us to obtain reliable intensities also in cases, where the widely used SA cannot be applied.

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