Correction: Dyson orbitals within the fc-CVS-EOM-CCSD framework: theory and application to X-ray photoelectron spectroscopy of ground and excited states

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An error was detected, and it is hereby corrected, in the computation of the photoelectron spectra obtained by ionizing core electrons of the two lowest excited states of uracil. A re-examination of the Hartree–Fock molecular orbitals in the 6-311(2+)+G** (uncontracted) basis (which was used in the calculations) has revealed that the SCF procedure did not converge to the desired lowest triplet states of nπ* and πn* characters, but instead found nRy and πRy solutions. While the character of the hole orbital in these states is the same as in the S₁ and S₂ states, the character of the particle orbital is different. Thus, the XPS reported in ref. 1 do not correspond to the XPS of the S₁ and S₂ excited states. This unfortunate problem occurred because of using a non-standard basis set (uncontracted), which affected the default guess in the SCF procedure. Because of the multiple diffuse functions present in the basis, the SCF calculation of the lowest triplet inadvertently converged to a Rydberg state instead of the valence state. This problem can be easily corrected by using molecular orbitals from the ground-state calculation together with the correct user-defined orbital occupation and the MOM algorithm.

The results of the calculations of the spectra with the correct orbital occupations are reported below. Fig. 1–3 show the amended spectra at the carbon, nitrogen, and oxygen K-edges, respectively. They replace Fig. 5–7 in the original article. Tables 1 and 2 summarize the raw data (ionization energies and squared Dyson orbital norms) for the S₁ and S₂ excited states, and amend the results in Tables 5 and 6 in the original article.

Below we present the amended discussion of the computed spectra. Importantly, the main conclusion of ref. 1 remains valid: The XPS spectroscopy on the oxygen edge can be used to distinguish different electronic states in uracil.

At all three edges, the XPS spectra of the two excited states are now found significantly closer to that of the ground state. In most cases, the binding energies of the core electrons are slightly red-shifted relative to the corresponding S₀ values, indicating a destabilization of the core electrons in the excited states.

At the C K-edge, see Fig. 1, the ordering of the A and B bands is reversed in the S₂ state, indicating the stabilization (higher binding energy) of the 1s electron of the C atom at position A and destabilization of the 1s electron of the C atom at position B.

At the N K-edge (cf. Fig. 2), the ordering of the A and B bands changes in the S₁ state, primarily due to a larger destabilization of the 1s electron of the N atom at position B than for the one at position A.

The significant overlap of the C and N edge spectra corresponding to the two excited states makes them less attractive probes since no specific spectral signature region emerges.

At the oxygen K-edge, see Fig. 3, substantial differences between the spectra of the three states (ground state, S₁ and S₂) are found. In line with the localized nature of the nπ* state (see Table 3 in ref. 1), the 1s electron of the oxygen in the A position is strongly stabilized in the S₁ state, versus a very modest destabilization of the one in B position, with a separation between the two IEs of 4–5 eV. This confirms our previous conclusion¹ that the oxygen K-edge region would be the most interesting edge for probing the excited-state dynamics of the S₁ state by UV-pump/XPS-probe spectroscopy.
Fig. 1  Uracil. C K-edge fc-CVS-EOM-CCSD/6-311(2+,+)-G** (uncontracted) X-ray photoelectron spectra of the ground state ($S_0$), first excited state ($S_1$, $\pi^*$), and second excited state ($S_2$, $\pi\pi^*$) corresponding to the ejection of either an $\alpha$ or a $\beta$ electron, obtained by convolution of the computed ionization energies and Dyson norms with a Lorentzian function (FWHM = 0.4 eV).

Table 1  Uracil. Ionization energies (IE, eV) and squared norms of Dyson orbitals for the first excited state ($S_1$). The results are reported at the Franck–Condon geometry (no label) and at state-specific zero-gradient, stationary point (label sp) geometry

| K-edge | $S_1$ | $S_1$ (sp) |
|--------|-------|-----------|
|        | IE    | $\phi^{Dyson}_x$ | $\phi^{Dyson}_x$ | IE    | $\phi^{Dyson}_x$ | $\phi^{Dyson}_x$ |
|        | $\alpha$ |       |       | $\beta$ |       |       | $\beta$ |       |       | $\beta$ |       |       | $\beta$ |
| Carbon  | 291.47 | 291.68 | 0.876 | 0.882 | 291.68 | 291.96 | 0.878 | 0.883 |
|        | 292.42 | 291.93 | 0.884 | 0.883 | 292.83 | 292.26 | 0.881 | 0.882 |
|        | 294.37 | 293.87 | 0.879 | 0.877 | 294.53 | 294.04 | 0.877 | 0.875 |
|        | 296.10 | 296.31 | 0.885 | 0.885 | 296.10 | 296.11 | 0.885 | 0.885 |
| Nitrogen | 407.15 | 407.08 | 0.880 | 0.881 | 407.34 | 407.28 | 0.879 | 0.880 |
|        | 407.63 | 407.48 | 0.877 | 0.879 | 407.59 | 407.48 | 0.877 | 0.879 |
| Oxygen  | 538.88 | 538.86 | 0.880 | 0.880 | 538.82 | 538.81 | 0.881 | 0.880 |
|        | 544.00 | 542.82 | 0.878 | 0.890 | 544.04 | 542.75 | 0.876 | 0.886 |

Table 2  Uracil. Ionization energies (IE, eV) and squared norms of the second excited state ($S_2$). The results are reported at the Franck–Condon geometry (no label) and at state-specific zero-gradient, stationary point (label sp) geometry

| K-edge | $S_2$ | $S_2$ (sp) |
|--------|-------|-----------|
|        | IE    | $\phi^{Dyson}_x$ | $\phi^{Dyson}_x$ | IE    | $\phi^{Dyson}_x$ | $\phi^{Dyson}_x$ |
|        | $\alpha$ |       |       | $\beta$ |       |       | $\beta$ |       |       | $\beta$ |       |       | $\beta$ |
| Carbon  | 292.98 | 292.34 | 0.883 | 0.886 | 293.12 | 292.48 | 0.878 | 0.881 |
|        | 293.27 | 292.60 | 0.879 | 0.883 | 293.58 | 292.94 | 0.870 | 0.875 |
|        | 294.94 | 295.04 | 0.879 | 0.880 | 295.08 | 295.24 | 0.872 | 0.875 |
|        | 296.35 | 296.37 | 0.883 | 0.883 | 296.30 | 296.32 | 0.882 | 0.881 |
| Nitrogen | 407.28 | 407.27 | 0.880 | 0.881 | 407.45 | 407.44 | 0.878 | 0.879 |
|        | 408.13 | 407.99 | 0.870 | 0.874 | 407.82 | 407.66 | 0.870 | 0.873 |
| Oxygen  | 539.32 | 539.27 | 0.877 | 0.878 | 539.11 | 539.11 | 0.878 | 0.877 |
|        | 539.57 | 539.29 | 0.882 | 0.885 | 539.64 | 539.64 | 0.888 | 0.888 |
The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

**Conflicts of interest**

The authors declare the following competing financial interest(s): A. I. K. is a part owner and a board member of Q-Chem, Inc.
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