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Dyson Orbitals<sup>†</sup>Marta L. Vidal,<sup>\*a</sup> Anna I. Krylov,<sup>b</sup> and Sonia Coriani<sup>a‡</sup>

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The abstract should be a single paragraph which summarises the content of the article. Any references in the abstract should be written out in full *e.g.* [Surname *et al.*, *Journal Title*, 2000, **35**, 3523].

## 1 Introduction

## 2 Theory

## 2.1 fc-CVS-EOM-CCSD?

In the EOM-CC approach, the target-state wave functions are parameterized using the following ansatz:<sup>1?–3</sup>

$$\langle \Psi_L | = \langle \Phi_0 | L e^{-T} ; \quad | \Psi_R \rangle = e^T R | \Phi_0 \rangle \quad (1)$$

In this work, we focus on the EOM-CCSD family of methods in which the cluster operator  $T$  is truncated after single (S) and double (D) excitations, and so are the excitation  $R$  and de-excitation  $L$  operators.

$$\langle \Phi_\mu | \bar{H} - E_{CC} | \Phi_0 \rangle = 0 ; \quad E_{CC} = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle \quad (2)$$

where  $\langle \Phi_\mu |$ 's represent  $\mu$ -tuple excited determinants and  $\bar{H}$  is the similarity transformed Hamiltonian:

$$\bar{H} = e^{-T} H e^T. \quad (3)$$

In the EOM-IP (EOM for ionization potentials) method<sup>???</sup>, the excitation operator changes the number of electrons in the system, assuming the following from:

$$R^{IP} = \sum_i r_i a_i + \frac{1}{4} \sum_{ija} r_{ij}^a a_a^\dagger a_j a_i + \dots \quad (4)$$

that allows to access the ionized state:

$$| \Psi_R^{N-1} \rangle = R^{IP} e^T | \Phi_0 \rangle \quad (5)$$

## 2.2 Dyson Orbitals

Dyson orbitals are defined for any two wave functions that differ by one electron as the overlap between an  $N$ -electron reference state and the  $N \pm 1$ -electron target state. In first quantization, the Dyson orbitals can be written as follows:

$$\phi_{if}^{Dyson}(x_1) = \sqrt{N} \int \Psi_i^N(x_1, x_2, \dots, x_N) \Psi_f^{N-1}(x_2, \dots, x_N) dx_2 \dots dx_N \quad (6)$$

In second quantization, they can be expanded over a set of the reference molecular orbitals  $\{\phi_p\}$ :

$$\phi_{if}^{Dyson}(x_1) = \sum_p \gamma_p \phi_p(x_1) \quad (7)$$

where the coefficients of the expansions take the following form for the right and left Dyson orbitals respectively:

$$\gamma_p^R = \langle \Psi^N | a_p^\dagger | \Psi^{N-1} \rangle \quad (8)$$

$$\gamma_p^L = \langle \Psi^{N-1} | a_p^\dagger | \Psi^N \rangle \quad (9)$$

The programmable expressions are given in the Supplementary Information, where each set of coefficient has been split into three different blocks; virtual, occupied valence (denoted with a  $v$  subindex) and occupied core (denoted with a capital later). It is possible to calculate photoelectron spectra from the norm of the Dyson orbitals. Indeed, the ionization yield is proportional to the Dyson norm, and although a more accurate treatment is possible, the Dyson norms can be taken as good approximation as a measure of the ionization intensities to simulate XPS spectra.

## 3 Computational details

For 9H-adenine, we considered the planar structure optimized at the B3LYP/cc-pVTZ level.<sup>4</sup> Experimental data was taken from Ref. 5 for adenine and thymine. All experimental spectra were digitized from the original references using WebPlotDigitizer<sup>6</sup>. The spectra were generated using a Python script and Dyson orbitals were visualized using MOLDEN<sup>7</sup>.

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<sup>†</sup> Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/cXCP00000x/

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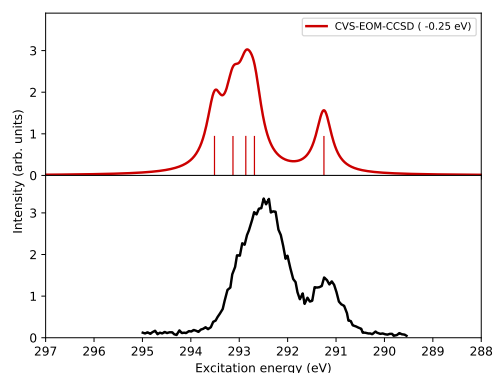
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## 4 Results and discussion

### 4.1 Adenine

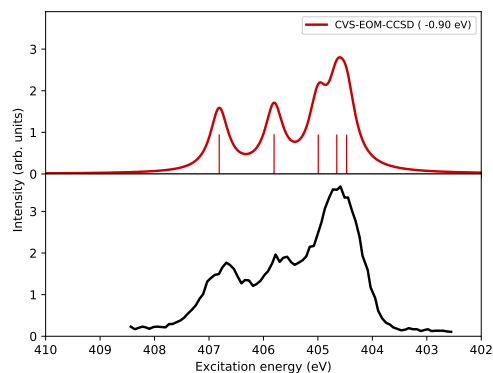
The X-ray photoelectron spectra of adenine are shown in Figure 1 and 2.

#### 4.1.1 C K-edge



**Fig. 1** Adenine. C K-edge fc-CVS-EOM-CCSD/6-311(2+,+) $G^{**}$  (uncontracted on C) X-ray photoelectron spectra obtained by convolution of the computed ionization energies and Dyson norms with a Lorentzian function (FWHM = 0.4 eV). The rigid shift applied is indicated in parenthesis in the legend. It was determined with respect to the first experimental peak position, estimated to be at 286.4 eV. The experimental spectra was digitized from Ref. 5.

#### 4.1.2 N K-edge



**Fig. 2** Adenine. N K-edge fc-CVS-EOM-CCSD/6-311(2+,+) $G^{**}$  (uncontracted on N) X-ray photoelectron spectra obtained by convolution of the computed ionization energies and Dyson norms with a Lorentzian function (FWHM = 0.4 eV). The rigid shift applied is indicated in parenthesis in the legend. It was determined with respect to the first experimental peak position, estimated to be at 399.4 eV. The experimental spectra was digitized from Ref. 5.

**Table 1** Adenine. C K-edge ionization energies (in eV) and DO norms obtained at the fc-CVS-EOM-CCSD/6-311(2+,+) $G^{**}$  (uncontracted on C) level of theory

IE	DO norm	DO	Exp. <sup>5</sup>
291.50	0.93425		291.0
292.94	0.93517		292.5
293.11	0.93635		
293.38	0.93349		
293.76	0.93611		

### 4.2 TR-XPS: Uracil

#### 4.2.1 C K-edge

#### 4.2.2 O K-edge

## 5 Conclusions

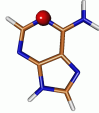
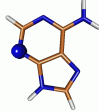
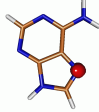
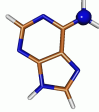
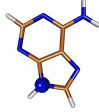
### Conflicts of interest

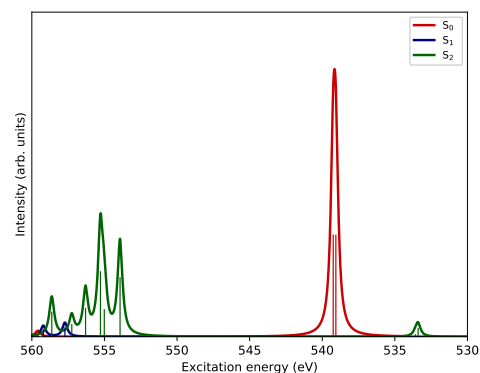
The authors declare the following competing financial interest(s): A.I.K. is a part owner and a board member of Q-Chem, Inc.

### Acknowledgements

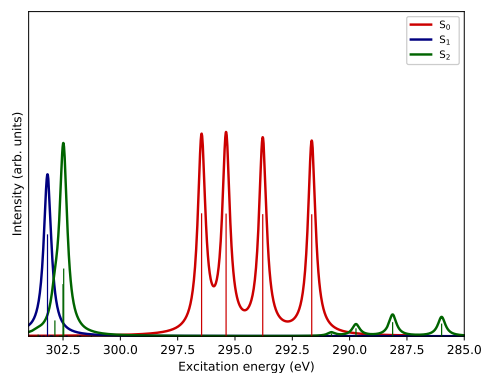
M.L.V. and S.C. acknowledge support from DTU Chemistry (start-up Ph.D. grant). S.C. acknowledges support from the Independent Research Fund Denmark – DFF-Forskningsprojekt2 grant no. 7014-00258B and from the H2020-MSCA-ITN-2017 training network “COSINE – Computational Spectroscopy In Natural sciences and Engineering”. A.I.K. acknowledges support by the U.S. National Science Foundation (No. CHE-1566428) and by the Simons Foundation.

**Table 2** Adenine. N K-edge ionization energies (in eV) and DO obtained at the fc-CVS-EOM-CCSD/6-311(2+,+)G\*\* (uncontracted on N) level of theory

IE	DO norm	DO	Exp. <sup>5</sup>
405.37	0.93367		404.4
405.55	0.93298		
405.89	0.93414		
406.70	0.93902		405.7
407.71	0.93721		406.7



**Fig. 4** Uracil. O K-edge fc-CVS-EOM-CCSD/6-311(2+,+)G\*\* (uncontracted) X-ray photoelectron spectra of the ground-state, first excited state ( $S_1$ ) and second excited state ( $S_2$ ) obtained by convolution of the computed ionization energies and Dyson norms with a Lorentzian function (FWHM = 0.4 eV).



**Fig. 3** Uracil. C K-edge fc-CVS-EOM-CCSD/6-311(2+,+)G\*\* (uncontracted) X-ray photoelectron spectra of the ground-state, first excited state ( $S_1$ ) and second excited state ( $S_2$ ) obtained by convolution of the computed ionization energies and Dyson norms with a Lorentzian function (FWHM = 0.4 eV).

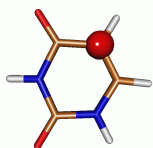
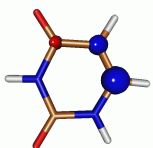
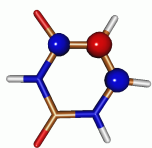
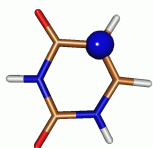
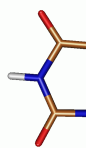
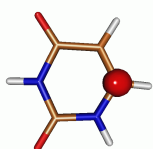
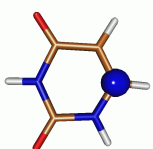
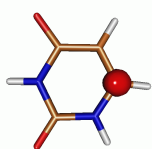
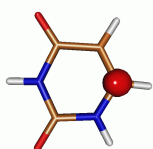
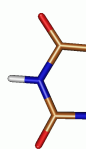
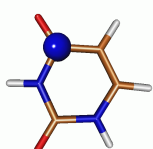
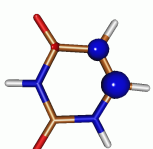
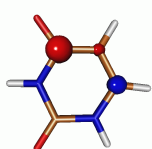
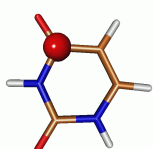
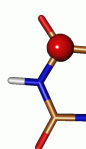
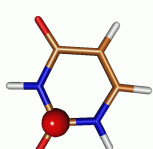
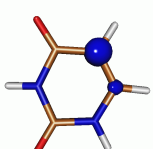
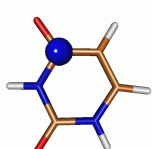
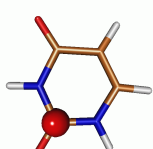
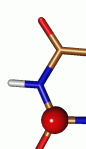
**Table 3** Uracil C K-edge. Ionization energies (eV) and DO norms of the GS, first ( $S_1$ ) and second ( $S_2$ ) excited states

Symm	$S_0$		$S_1$		$S_2$	
	IE	DO norm	IE	DO norm	IE	DO norm
A'	291.65	0.93461	286.50	0.000000	285.99	0.092479
A'	293.79	0.93539	288.64	0.000000	288.12	0.103488
A'	295.39	0.93984	290.24	0.000000	289.72	0.056248
A'	296.46	0.94187	291.31	0.000000	290.79	0.016696
A'	306.93	0.00005	301.78	0.000000	301.26	0.000453
A'	307.52	0.00011	302.37	0.000000	301.85	0.001440
A'	308.14	0.03951	302.99	0.000000	302.47	0.516492
A'	308.17	0.05949	303.02	0.000000	302.50	0.396508
A''	308.19	0.00000	303.03	0.002360	302.52	0.000000
A'	308.22	0.00007	303.07	0.000000	302.56	0.000245
A''	308.33	0.00000	303.18	0.779799	302.66	0.000000
A'	308.52	0.02467	303.37	0.000000	302.86	0.116798
A'	308.68	0.00009	303.53	0.000000	303.02	0.000493
A'	309.25	0.00145	304.10	0.000000	303.59	0.007250

**Table 4** Uracil O K-edge. Ionization energies (eV) and DO norms of the GS, first ( $S_1$ ) and second ( $S_2$ ) excited states

Symm	$S_0$		$S_1$		$S_2$	
	IE	DO norm	IE	DO norm	IE	DO norm
A'	539.06	0.93739	533.92	0.000000	533.40	0.075477
A'	539.24	0.93867	534.10	0.000000	533.58	0.017569
A'	559.04	0.00001	553.90	0.000000	553.38	0.000048
A'	559.59	0.03367	554.45	0.000000	553.92	0.545201
A'	560.21	0.00000	555.07	0.000000	554.55	0.000016
A'	560.67	0.02111	555.53	0.000000	555.01	0.249325
A'	560.94	0.02493	555.80	0.000000	555.27	0.600162
A'	561.96	0.01137	556.82	0.000000	556.30	0.259845
A'	562.20	0.00009	557.05	0.000000	556.53	0.000224
A''	562.79	0.00000	557.65	0.000046	557.13	0.000000
A''	562.86	0.00000	557.72	0.081796	557.20	0.000000
A'	562.91	0.02313	557.77	0.000000	557.25	0.111828
A'	564.29	0.01974	559.15	0.000000	558.63	0.226836
A''	564.35	0.00000	559.21	0.063712	558.69	0.000000
A'	564.73	0.00030	559.58	0.000000	559.06	0.000247

**Table 5** Uracil. fc-CVS-EOM-CCSD/6-311(2+,+)G\*\* DOs of the first core-ionized states. DO isosurface is 0.05

State	$S_0$	$S_1$	$S_{1(sp)}$	$S_2$	$S_{2(sp)}$
1					
2					
3					
4					

The main text of the article<sup>?</sup> should appear here.

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Section headings can be typeset with and without numbers.<sup>?</sup>

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## 6 Graphics and tables

### 6.1 Graphics

Graphics should be inserted on the page where they are first mentioned (unless they are equations, which appear in the flow of the text).<sup>?</sup>

**Fig. 5** An example figure caption – the image is from the *Physical Chemistry Chemical Physics* cover gallery.

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**Table 6** An example of a caption to accompany a table

Header one (units)	Header two	Header three
1	2	3
4	5	6
7	8	9
10	11	12

Adding notes to tables can be complicated. Perhaps the easiest method is to generate these manually.<sup>§</sup>

## 7 Equations

Equations can be typeset inline *e.g.*  $y = mx + c$  or displayed with and without numbers:

$$A = \pi r^2$$
$$\frac{\gamma}{\epsilon x} r^2 = 2r \quad (10)$$

You can also put lists into the text. You can have bulleted or numbered lists of almost any kind. The `mhchem` package can also be used so that formulae are easy to input: `\ce{H2SO4}` gives H<sub>2</sub>SO<sub>4</sub>.

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## 8 Conclusions

The conclusions section should come in this section at the end of the article, before the Conflicts of interest statement.

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## Acknowledgements

The Acknowledgements come at the end of an article after Conflicts of interest and before the Notes and references.

## Notes and references

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§ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

**Fig. 6** An image from the *Physical Chemistry Chemical Physics* cover gallery, set as a two-column figure.

**Table 7** An example of a caption to accompany a table – table captions do not end in a full point

Header one	Header two	Header three	Header four	Header five	Header six	Header seven
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15	16	17	18	19	20	21