

Supplemental material for the paper: Absolute binding energies of core levels in solids from first-principles

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1 Calculated binding energies of core levels in gaseous systems

Contrary to the bulk systems, for gaseous systems the common chemical potential does not exist anymore, and instead both vacuum levels of the sample and the spectrometer are aligned to zero by using a known ionization potential of a noble gas measured at the same time [1]. Then, the absolute binding energy $E_b^{(\text{gas})}$ is expressed by

$$E_b^{(\text{gas})} = E_f^{(0)}(N - 1) - E_i^{(0)}(N).$$

The binding energies of a core level for gaseous molecules calculated by using the above equation are shown in Table S-I, where the mean absolute (relative) error is found to be 0.5 eV (0.22 %) for the 23 cases. The underestimation of splittings in a O_2 and NO molecule should be attributed to an insufficient treatment of the exchange interaction in the semi-local functional rather than the proposed method, suggesting the necessity of non-local functionals for an accurate description of the intra-atomic exchange interaction [6].

TABLE S-I. Calculated binding energies of core levels in gaseous systems. The Si-2*p* states were calculate by a scalar relativistic treatment [7]. The non-equivalent nitrogen atoms in a N₂O molecule are specified by the underline.

Molecule	Calc. (eV)	Expt.* (eV)
<i>C-1s state</i>		
CO	295.87	296.19
C ₂ H ₂	291.24	291.17
CO ₂	296.89	297.66
HCN	293.35	293.50
C ₂ H ₄	290.50	290.79
H ₂ CO	294.00	294.47
<i>N-1s state</i>		
N ₂	409.89	409.83
NH ₃	404.70	405.60
N ₂ H ₄	404.82	406.1
HCN	406.16	406.36
<u>N</u> NO	408.24	408.66
N <u>N</u> O	411.98	412.57
NO(S=0)	410.62	411.6
NO(S=1)	410.10	410.2
<i>O-1s state</i>		
CO	542.50	542.4
CO ₂	541.08	541.2
O ₂ (S= $\frac{1}{2}$)	543.15	544.2
O ₂ (S= $\frac{3}{2}$)	542.64	543.1
H ₂ O	539.18	539.9
<i>Si-2p state</i>		
SiH ₄	106.56	107.3
Si ₂ H ₆	106.21	106.86
SiF ₄	111.02	111.7
SiCl ₄	109.32	110.2

* [2, 3, 4, 5]

2 Details of implementation

The proposed method has been implemented in a DFT software package OpenMX [8], which is based on norm-conserving relativistic pseudopotentials [9, 10] and pseudo-atomic basis functions [11]. The pseudopotentials were generated including the $1s$ -state for a carbon, nitrogen, and oxygen atom, and up to the $2p$ -states for a silicon atom [9, 10], respectively, by solving the spherical Dirac equation. In the pseudopotential generation, the occupation of the state for which a core hole is created in the final state calculations is reduced by 0.5, and the remaining occupation is added to that of the valence states. The pseudopotentials were commonly used in the calculations for the initial and final states. The treatment for the occupation in generating the pseudopotentials might be a non-biased way in applying pseudopotentials for the initial and final states on equal footing. The Kohn-Sham wave functions are expressed by a two-component spinor, and the spatial part is expanded by a linear combination of pseudo-atomic orbitals (PAOs). As basis functions of PAOs variationally optimized double valence plus single polarization orbitals (DVSP) and triple valence plus double polarization orbitals (TVDP) were used for bulks and gaseous molecules, respectively, after careful benchmark calculations for the convergence [11, 13]. The spin-orbit coupling was taken into account self-consistently through the j -dependent relativistic pseudopotentials [9, 10]. Neither a frozen core approximation nor any restriction for spin polarization were introduced for the core state for which a core hole is created in the final state calculations. A generalized gradient approximation (GGA) [12] to the exchange-correlation functional was used. It was assumed that electrons populate the Kohn-Sham eigenstates according to the Fermi distribution at a finite temperature, resulting the self-consistent determination of the chemical potential μ_0 depending on the band gap and shape of density of states. For all the calculations in the study we used an electronic temperature of 300 K. In all the cases we used the chemical potential μ_0 calculated for the initial state without a core hole for Eq. (3). The real space grid techniques were used with the energy cutoff of 350 Ry in numerical integrations and the solution of Poisson equation using FFT [14].

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