Supporting Information for "Kohn–Sham decomposition in real-time time-dependent density-functional theory: An efficient tool for analyzing plasmonic excitations"

T. P. Rossi,[1,*] M. Kuisma,[2,3,†] M. J. Puska,[1] R. M. Nieminen,[1] and P. Erhart[2,‡]

[1] *COMP Centre of Excellence, Department of Applied Physics, Aalto University School of Science, Espoo, Finland*

[2] *Department of Physics, Chalmers University of Technology, Gothenburg, Sweden*

[3] *Department of Chemistry, Nanoscience Center, University of Jyväskylä, Jyväskylä, Finland*

[*] tuomas.rossi@alumni.aalto.fi [†] mikael.j.kuisma@jyu.fi [‡] erhart@chalmers.se

S1 Derivation of Eq. (9) within the PAW formalism

Within the PAW formalism [P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994)], Eq. (1) reads

$$i\mathcal{T}^\dagger\mathcal{T}\frac{\partial}{\partial t}\widetilde{\psi}_n(\boldsymbol{r},t) = \mathcal{T}^\dagger H_{\mathrm{KS}}(t)\mathcal{T}\widetilde{\psi}_n(\boldsymbol{r},t), \tag{S1}$$

where $\widetilde{\psi}_n(\boldsymbol{r},t)$ is a pseudo wave function and $\mathcal{T}$ denotes the PAW transformation operator.

In the LCAO method, the pseudo wave function $\widetilde{\psi}_n(\boldsymbol{r},t)$ is expanded in localized basis functions $\widetilde{\phi}_\mu(\boldsymbol{r})$ centered at atomic coordinates

$$\widetilde{\psi}_n(\boldsymbol{r},t) = \sum_\mu \widetilde{\phi}_\mu(\boldsymbol{r})C_{\mu n}(t), \tag{S2}$$

with expansion coefficients $C_{\mu n}(t)$. The corresponding all-electron wave function is given by [compare to Eq. (7)]

$$\psi_n(\boldsymbol{r},t) = \mathcal{T}\widetilde{\psi}_n(\boldsymbol{r},t) = \sum_\mu \phi_\mu(\boldsymbol{r})C_{\mu n}(t), \tag{S3}$$

where the all-electron basis functions have been defined as $\phi_\mu = \mathcal{T}\widetilde{\phi}_\mu$.

The time-dependent all-electron real-space KS density matrix can be obtained as

$$\rho(\boldsymbol{r},\boldsymbol{r}',t) = \sum_{\mu\nu}\phi_\mu(\boldsymbol{r})\rho_{\mu\nu}(t)\phi^*_\nu(\boldsymbol{r}'), \tag{S4}$$

where the KS density matrix in the LCAO basis $\rho_{\mu\nu}(t)$ is given by Eq. (8).

The transformation of the real-space KS density matrix to the basis defined by the ground-state KS orbitals $\psi^{(0)}_n(\boldsymbol{r})$, see Eq. (3), is given by

$$\rho_{nn'}(t) = \int \mathrm{d}\boldsymbol{r}\int \mathrm{d}\boldsymbol{r}'\psi^{(0)*}_n(\boldsymbol{r})\rho(\boldsymbol{r},\boldsymbol{r}',t)\psi^{(0)}_{n'}(\boldsymbol{r}'). \tag{S5}$$

By expanding $\psi^{(0)}_n(\boldsymbol{r})$ in the LCAO basis as in Eq. (S3) and inserting Eq. (S4) into Eq. (S5), we obtain after reordering the integrals

$$\rho_{nn'}(t) = \sum_\mu C^{(0)*}_{\mu n}\sum_{\mu'}\underbrace{\int \mathrm{d}\boldsymbol{r}\phi^*_\mu(\boldsymbol{r})\phi_{\mu'}(\boldsymbol{r})}_{S_{\mu\mu'}} \cdot\sum_{\nu'}\rho_{\mu'\nu'}(t)\sum_\nu\underbrace{\int \mathrm{d}\boldsymbol{r}'\phi^*_{\nu'}(\boldsymbol{r}')\phi_\nu(\boldsymbol{r}')}_{S^*_{\nu\nu'}}C^{(0)}_{\nu n'}. \tag{S6}$$

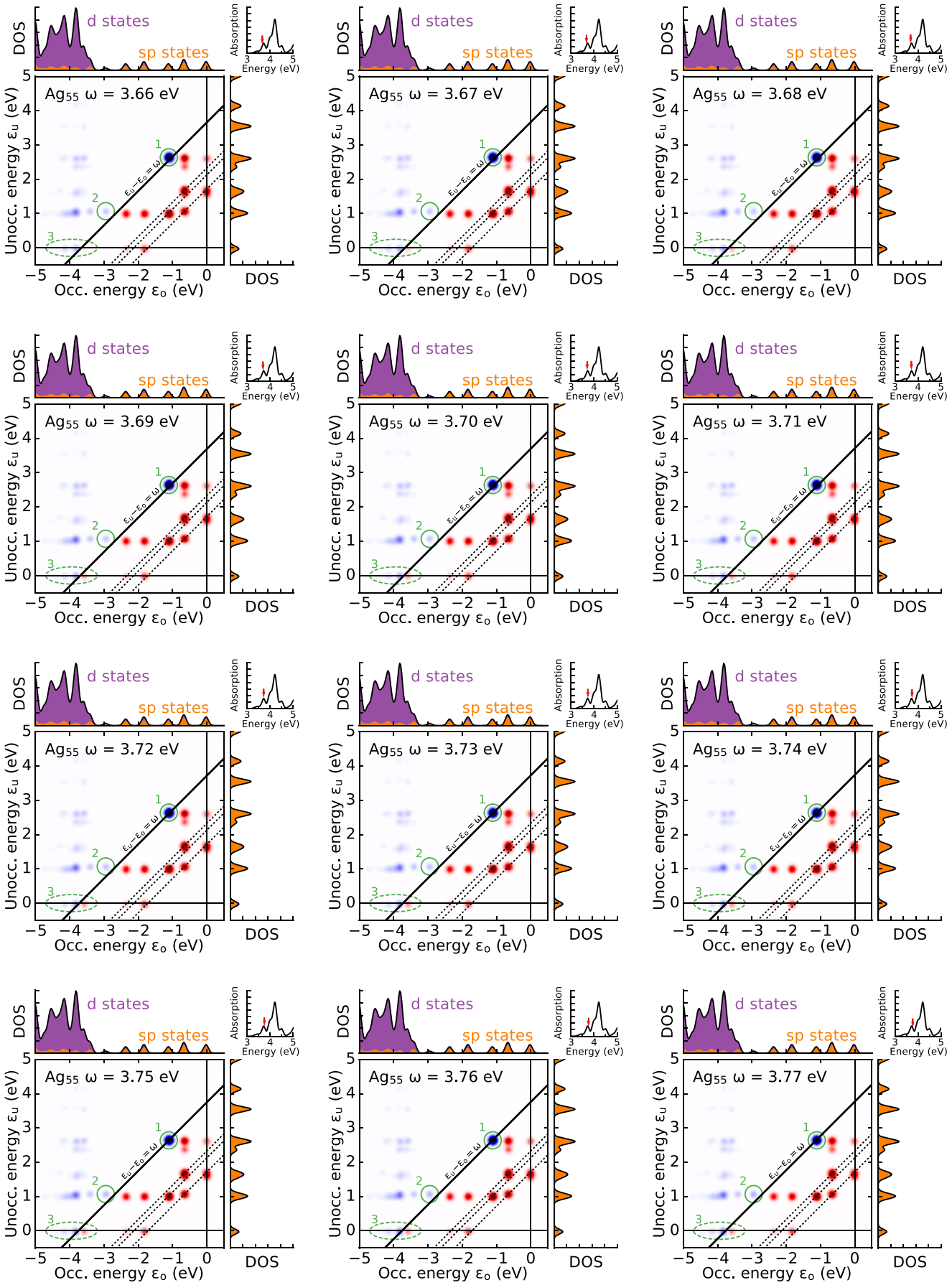
Here, we have isolated the overlap integrals $S_{\mu\mu'}$ used regularly in LCAO calculations, *i.e.*,

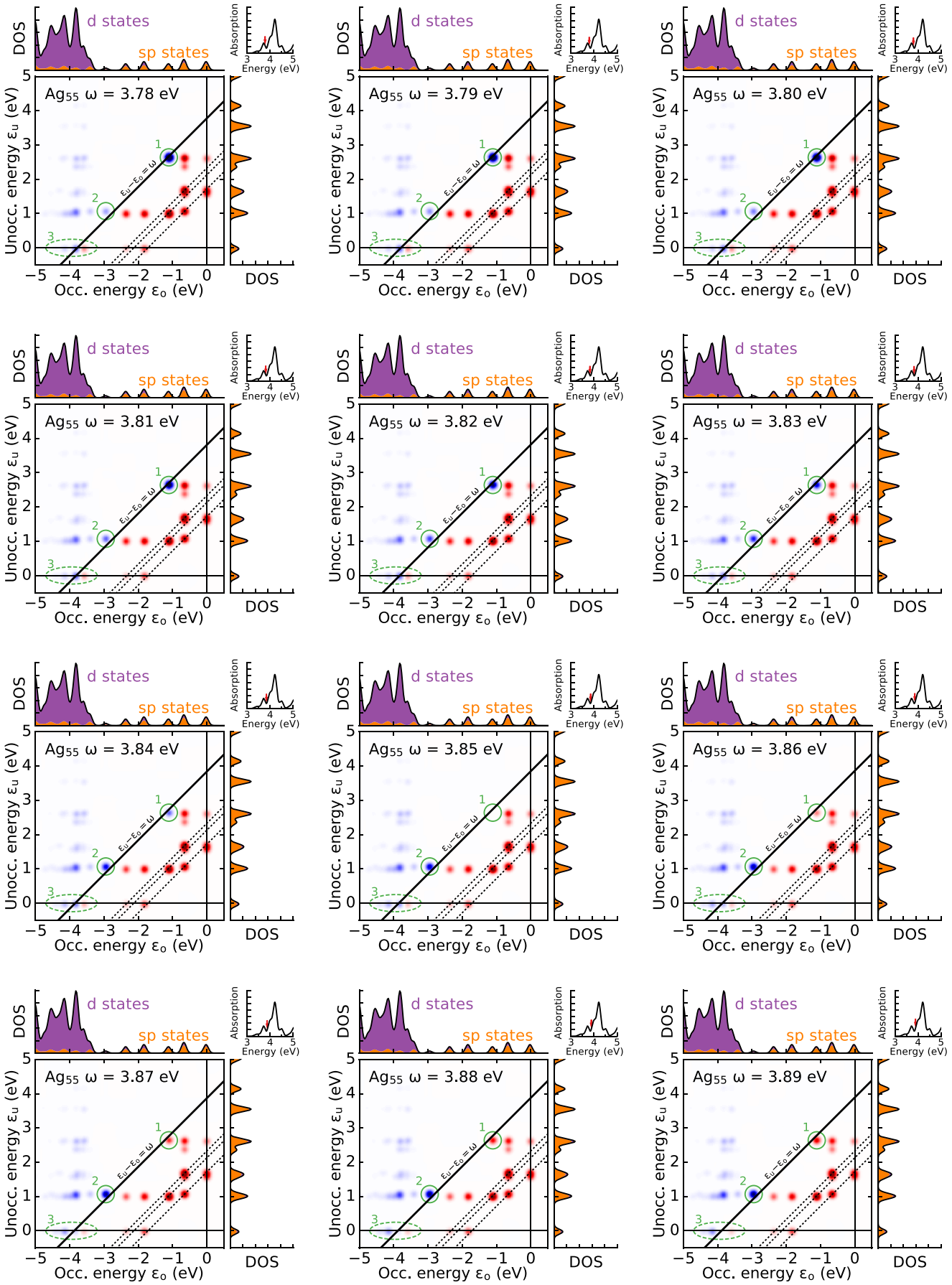
$$S_{\mu\mu'} = \int \mathrm{d}\boldsymbol{r}\phi^*_\mu(\boldsymbol{r})\phi_{\mu'}(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}\widetilde{\phi}^*_\mu(\boldsymbol{r})\mathcal{T}^\dagger\mathcal{T}\widetilde{\phi}_{\mu'}(\boldsymbol{r}). \tag{S7}$$

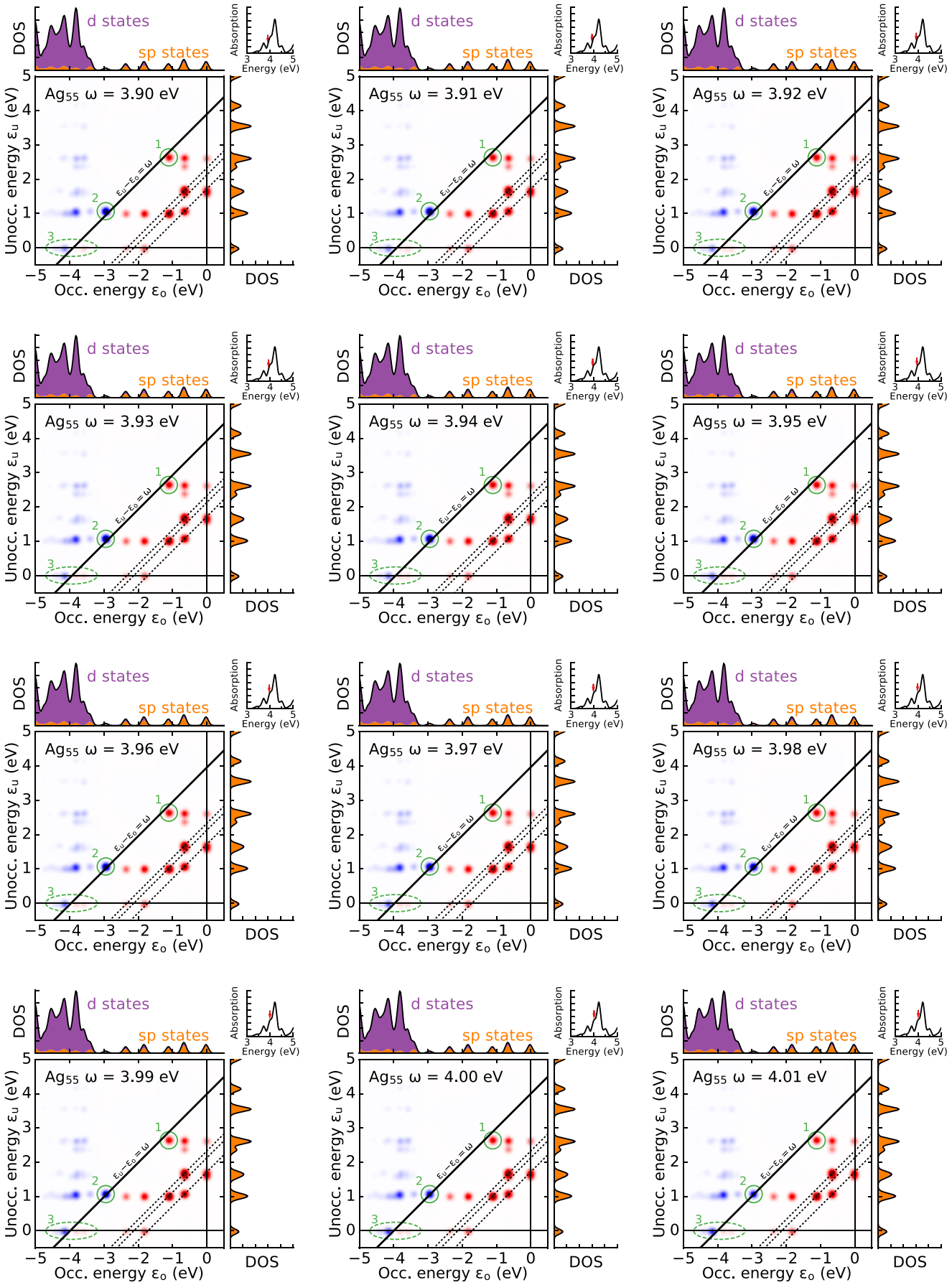
After simplifying the overlap integrals in Eq. (S6), we obtain Eq. (9). We note that the PAW transformation affects only the evaluation of the overlap integrals $S_{\mu\mu'}$, see Eq. (S7).

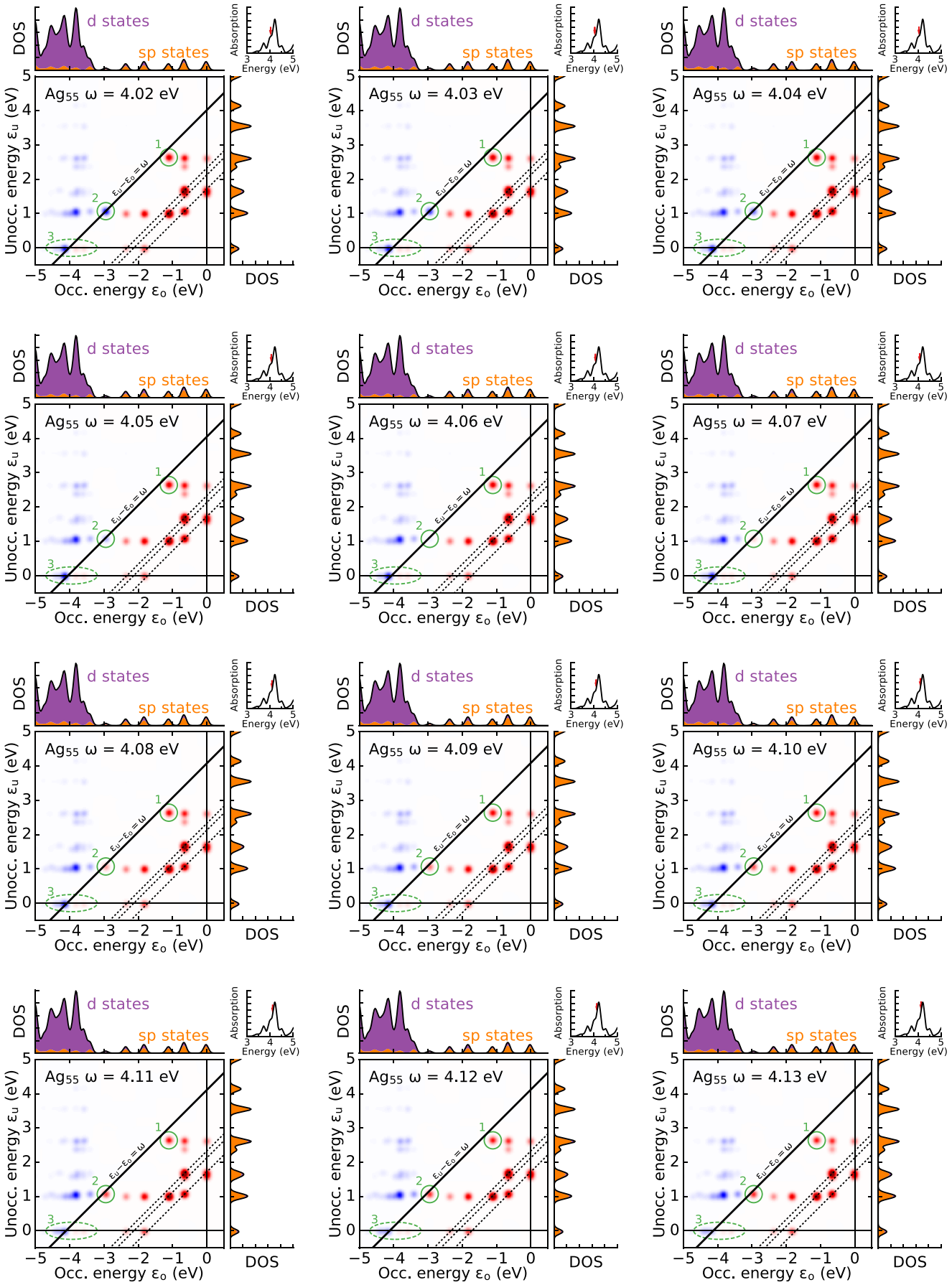
S2 Additional transition contribution maps for Ag_{55}

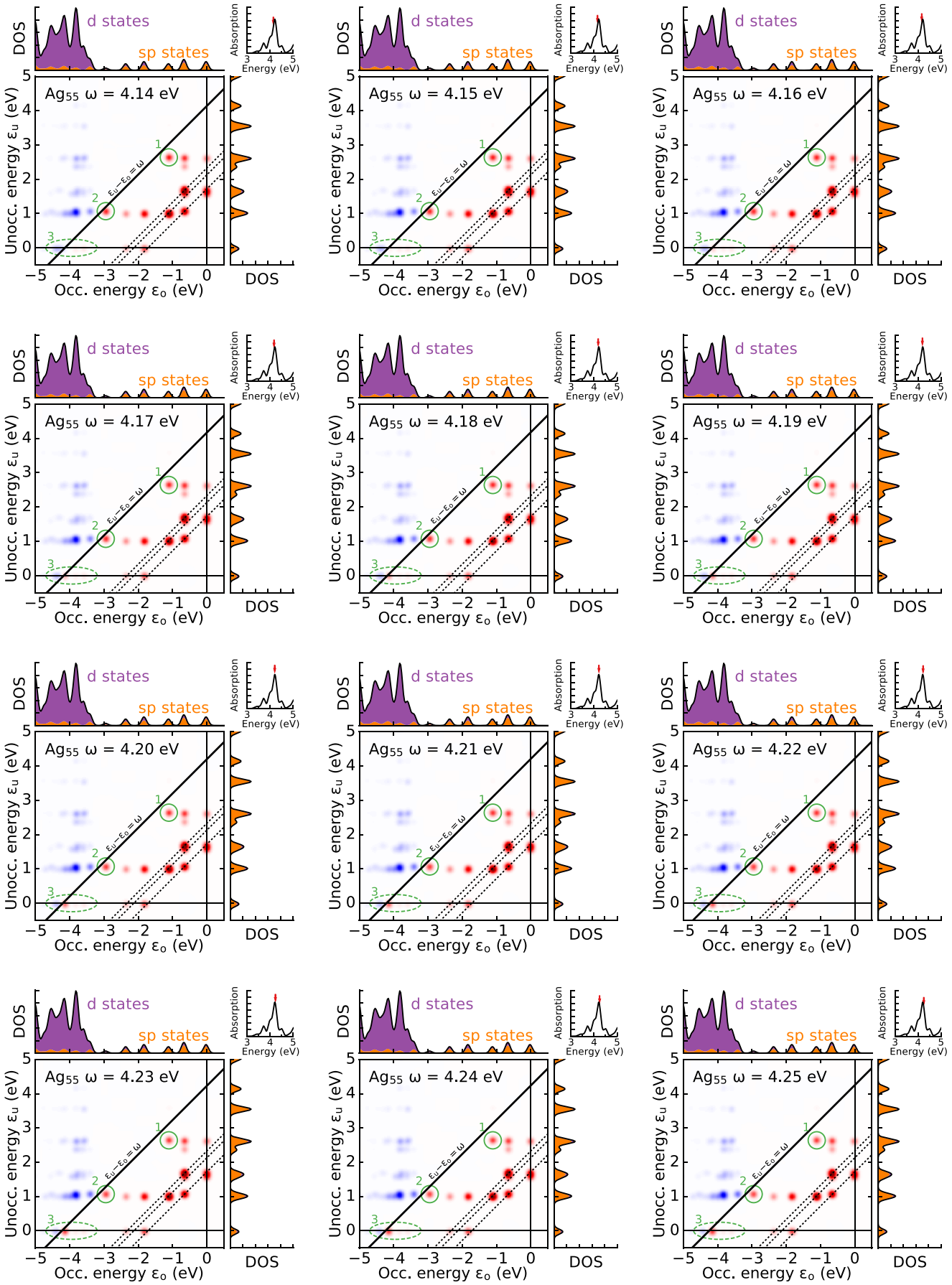
On the following pages, we present the transition contribution maps (TCMs) for the Ag_{55} nanoparticle from $\omega = 3.66\,\mathrm{eV}$ to $\omega = 4.25\,\mathrm{eV}$ in steps of $0.01\,\mathrm{eV}$. All TCMs use the same color scale (see the main text for definitions).


d states
sp states
DOS
Absorption
Energy (eV)
Ag55 ω = 3.66 eV
Ag55 ω = 3.67 eV
Ag55 ω = 3.68 eV
Ag55 ω = 3.69 eV
Ag55 ω = 3.70 eV
Ag55 ω = 3.71 eV
Ag55 ω = 3.72 eV
Ag55 ω = 3.73 eV
Ag55 ω = 3.74 eV
Ag55 ω = 3.75 eV
Ag55 ω = 3.76 eV
Ag55 ω = 3.77 eV
Unocc. energy εu (eV)
Occ. energy εo (eV)
εu−εo = ω
1
2
3


d states
sp states
DOS
Absorption
Energy (eV)
Ag55 ω = 3.78 eV
Ag55 ω = 3.79 eV
Ag55 ω = 3.80 eV
Ag55 ω = 3.81 eV
Ag55 ω = 3.82 eV
Ag55 ω = 3.83 eV
Ag55 ω = 3.84 eV
Ag55 ω = 3.85 eV
Ag55 ω = 3.86 eV
Ag55 ω = 3.87 eV
Ag55 ω = 3.88 eV
Ag55 ω = 3.89 eV
Unocc. energy εu (eV)
Occ. energy εo (eV)
εu−εo = ω
1
2
3


d states
sp states
DOS
Absorption
Energy (eV)
Ag55 ω = 3.90 eV
Ag55 ω = 3.91 eV
Ag55 ω = 3.92 eV
Ag55 ω = 3.93 eV
Ag55 ω = 3.94 eV
Ag55 ω = 3.95 eV
Ag55 ω = 3.96 eV
Ag55 ω = 3.97 eV
Ag55 ω = 3.98 eV
Ag55 ω = 3.99 eV
Ag55 ω = 4.00 eV
Ag55 ω = 4.01 eV
Unocc. energy εu (eV)
Occ. energy εo (eV)
εu−εo = ω
1
2
3


d states
sp states
DOS
Absorption
Energy (eV)
Ag55 ω = 4.02 eV
Ag55 ω = 4.03 eV
Ag55 ω = 4.04 eV
Ag55 ω = 4.05 eV
Ag55 ω = 4.06 eV
Ag55 ω = 4.07 eV
Ag55 ω = 4.08 eV
Ag55 ω = 4.09 eV
Ag55 ω = 4.10 eV
Ag55 ω = 4.11 eV
Ag55 ω = 4.12 eV
Ag55 ω = 4.13 eV
Unocc. energy εu (eV)
Occ. energy εo (eV)
εu−εo = ω
1
2
3


DOS
d states
sp states
Absorption
Energy (eV)
Ag55 ω = 4.14 eV
Ag55 ω = 4.15 eV
Ag55 ω = 4.16 eV
Ag55 ω = 4.17 eV
Ag55 ω = 4.18 eV
Ag55 ω = 4.19 eV
Ag55 ω = 4.20 eV
Ag55 ω = 4.21 eV
Ag55 ω = 4.22 eV
Ag55 ω = 4.23 eV
Ag55 ω = 4.24 eV
Ag55 ω = 4.25 eV
Unocc. energy εu (eV)
Occ. energy εo (eV)
εu−εo = ω
1
2
3