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Features of chemical bonds based on the overlap polarizabilities: diatomics and solid-state systems with the frozen-density embedding approach

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The chemical bond overlap properties were obtained for alkali halides NaY (Y = F, Cl, Br), alkaline-earth chalcogenides MX (M = Ca, Mg and X = O, S, Se) and alkali and alkali-earth metals (Li, Na, and Mg) in diatomic and solid-state systems using an embedding approach based on the Frozen Density Functional Theory to simulate the crystalline effects. The computational protocol established provides errors for bond distances smaller than 1% and the results indicate that more covalent chemical bonds lead to larger absorption or scattering by the overlap region. The ionic specific valence and overlap polarizability are closely related to the valence orbitals compactness measured by the sum of Mulliken electronegativities. The embedding approach used in this work makes it possible to quantify the effects of the crystalline environment on the chemical bond overlap properties. In solid-state, the bond overlap charges are less polarizable, in cases of well-known ionic systems (provided by electronegativity differences), being the chemical bonds less covalent in solids than in diatomic. The spectroscopic properties of the polarizability of the electron density in the overlap region of a chemical bond could be measured in the 1–20 eV spectral region and could be used to characterize some bands in several spectra whose assignments are ambiguous or not available.

Overlap integrals obtained self-consistently

For an open-shell system:

$$
\begin{aligned}
S_{ij} &= \int \sum_k a_k \phi_k s_k \cdot \sum_l b_l \phi_l s_l \, dr\, ds \\
&= \int \sum_k \sum_l a_k \phi_k s_k b_l \phi_l s_l \, dr\, ds \\
&= \sum_k \sum_l a_k b_l \int \phi_k \phi_l \, dr \int s_k s_l \, ds \\
&= \sum_k \sum_l a_k b_l \underbrace{\int \phi_k \phi_l \, dr}_{=O_{kl}} \left[\int \underbrace{s_k(\alpha) s_l(\alpha)}_{=1} + \underbrace{s_k(\alpha) s_l(\beta)}_{=0} + \underbrace{s_k(\beta) s_l(\alpha)}_{=0} + \underbrace{s_k(\beta) s_l(\beta)}_{=1} ds \right] \\
&= \sum_k \sum_l \left(a_k^{\alpha} b_l^{\alpha} + a_k^{\beta} b_l^{\beta} \right) O_{kl} \\
S_{ij} &= \sum_k \sum_l \left(a_k^{\alpha} b_l^{\alpha} + a_k^{\beta} b_l^{\beta} \right) O_{kl}
\end{aligned}
$$

Eq.S1

and for a closed-shell system:

$$S_{ij} = \sum_k \sum_l \left(a_k^{\alpha} b_l^{\alpha} + a_k^{\beta} b_l^{\beta} \right) O_{kl} \qquad \text{Eq.S2}$$

where a_k^{α}, b_l^{α}, a_k^{β} and b_l^{β} are the coefficients of the basis function centered at atoms A and B, with spins α and β, and O_{kl} is the overlap integral between the valence basis functions *k* and *l*.

Calculated values of underlying properties of the overlap charge density model

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Table S1. Underlying overlap density and chemical bond quantities. The experimental and calculated interatomic distances Rexp and Rcalc (Å); the gradient at minimum $\partial E/\partial R$ (Eh Å^{-1}); the overlap ρ; the second derivative of energy in respect to the distance $\partial^2 E/\partial^2 R$ and the coefficient of a fitted quadratic polynomial 2×B_2 (Eh Å^{-2}) at the minimum distance; the force constant k (10^5 dyn cm^{-1}); and the lowest excitation energy Δε (eV).

Crystal	R_{exp}	R_{calc}	$\partial E/\partial R$	ρ	$\partial^2 E/\partial^2 R$	2×B_2	k	Δε
NaF	2.307	2.318	1×10−4	0.1216	0.178	0.177	0.771	8.347
NaCl	2.810	2.818	2×10−5	0.1124	0.102	0.118	0.514	5.266
NaBr	2.980	3.016	1×10−4	0.0841	0.072	0.080	0.346	5.143

Table S2. Underlying overlap density and chemical bond quantities for alkali-earth chalcogenides and metals. The experimental and calculated interatomic distances R_{exp} and R_{calc} (Å); the relative error ER (%); the overlap ρ, the force constant k (10^5 dyn cm^{-1}); and the lowest excitation energy Δε (eV).

Crystal	R_{exp}	R_{calc}	ER	ρ	k	Δε
CaO	2.401	2.457	2.33	0.491	1.707	4.189
CaS	2.840	2.893	1.87	0.650	0.861	3.337
CaSe	2.963	3.016	1.79	0.668	1.384	3.722
MgO	2.107	2.147	1.87	0.818	1.540	7.042
MgS	2.600	2.665	2.50	0.873	0.869	3.990
MgSe	2.732	2.793	2.25	1.233	0.957	4.328
Li	3.040	2.988	-1.70	0.864	0.199	1.469
Na	3.724	3.575	-4.00	0.706	0.081	1.406
Mg	3.208	3.297	2.77	1.753	0.316	1.876

Table S3. Underlying overlap density and chemical bond quantities for alkali halide, alkali-earth chalcogenide and alkali diatomic molecules. The experimental and calculated interatomic distances R_{exp} and R_{calc} (Å); the relative error ER (%); the overlap ρ, the force constant k (10^5 dyn cm^{-1}); and the lowest excitation energy Δε (eV).

Diatomic	R_{exp}	R_{calc}	ER	ρ	k	Δε
NaF	1.926	2.000	3.84	0.119	1.455	2.657
NaCl	2.361	2.436	3.18	0.112	0.920	2.597
NaBr	2.502	2.589	3.47	0.081	0.771	2.429
CaO	1.822	1.875	2.90	0.193	3.004	1.113
CaS	2.318	2.355	1.60	0.521	1.892	1.025
CaSe		2.490		0.584	1.610	0.940
MgO	1.748	1.780	1.80	0.847	3.322	0.696
MgS		2.196		1.107	1.927	0.593
MgSe		2.325		1.406	1.599	0.508
LiLi	2.673	2.709	1.35	0.950	0.227	1.905
NaNa	3.079	3.096	0.55	0.867	0.154	2.075
MgMg	3.891	4.482	15.2	0.790	0.002	3.647

Notes and references

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