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Accurate defect formation energies in molecular materials

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All materials contain defects. Simulations are useful for predicting their concentration and resultant chemical behavior. In the subset of materials constructed from molecules, the conventional approach introduces avoidable errors stemming from how we treat the formation enthalpy of molecules. To compute defect energetics in molecular materials, a thoughtful treatment of molecular phase space is required. Here, we discuss strategies that account for the nuances of covalent chemical bonding.

Defects in molecular materials

Material defects can alter the characteristics of substances, imparting functionality beyond the confines of the periodically repeating unit cell. In the condensed phase, strategic control of defect concentrations will always be critically important, as the number and type of defects will determine the chemical reactivity, material conductivity, and other key properties [1]. Solid-state chemistry continues to evolve, with increasing reports of materials with designer properties, gleaned from preassembled molecular building blocks. In those materials there are other thermodynamic driving forces at play, as portions of the structure are held together with both covalent and intermolecular bonds. Unlike conventional defect sources (i.e., phases competing to provide or extract atoms from the crystal), molecules exist on a kinetic landscape and thus can be very far away from the phases of their thermodynamic constituents but trapped in deep potential wells. This can give rise to non-physical predictions of defect formation energies. Treating these intricacies requires thoughtful computational approaches and approximations based on chemical intuition and experiments.

Equilibrium defect formation energetics

Equilibrium defect formation energies [$E_f(D^q)$] are computed by selecting an *ab initio* method (e.g., an appropriate density functional) and then performing a series of calculations to solve for the formation energy of a defect, D, in charge state, q, through the relationship

$$E_f(D^q) = E_{tot}(D^q) - E_{tot}(\text{bulk}) + \sum_{n_i} n_i\mu_i + qE_F + E_{corr}, \quad [1]$$

where $E_{tot}(D^q)$ and $E_{tot}(\text{bulk})$ are the total internal energies of the defective material and pristine material, respectively. $\sum_{n_i} n_i\mu_i$ is the chemical potential term that denotes the energy of exchanging defective species with the bath of reactants or products (by convention interstitials have additive potentials, while vacancies are subtracted). E_F is the Fermi level and may be any numerical value spanning the electronic band gap. E_{corr} is a computational correction term needed for charged defects [2]. While E_F depends on the *ab initio* method, here we limit our discourse to exploring efforts to treat the chemical potential and correctional terms in molecular materials.

The chemical potential term is critical because it reflects the energy cost or gain associated with adding or removing atoms or molecules from the defective material. Formally, a complete treatment of this term requires sampling of all possible competing equilibrium phases composed of the atoms within the system. However, for molecular materials comprising C, N, O, and H, there are countless compositions, spanning a range of potentials. One strategy to narrow this chemical space is to use detected impurity and obvious kinetically competing phases.

With infinitely large cells, the correctional term reduces to zero. For smaller repeating models, charged defects may interact with their images in neighboring unit cells, crossing periodic boundaries. Such interactions may be real, while others may lead to artificial periodic self-interactions. To mitigate the fictitious portion of this interaction, and compute defect formation at the dilute limit, a finite-size correction must be implemented. Molecules present new challenges as their electronic states are highly localized, giving rise to large potential flux. Some correctional approaches are better suited to handle this.

Chemical potentials for molecules

To be comprehensive, one must consider the energetics of all phases that can form in a reaction mixture. As an example, Pb apatite (a molecularly linked network, Figure 1A) forms in a daunting phase space [3]. $Cu_{Pb}^{\times}$ substitutional defects may be introduced during synthesis by providing a Cu-source. In 'Pb-poor' conditions, the potential incentivizes the requisite Pb vacancy, while 'Cu-rich' conditions incentivize the requisite interstitial. One can make an approximation that Cu-defects in Pb apatite may form somewhere between μ_{Cu}(Cu) and μ_{Cu}(CuO), and μ_{Pb}(PbO) and μ_{Pb}(Pb). But the phase space becomes staggeringly complex for molecular materials and, in this case of Pb apatite, we have entirely omitted the inpact of phases formed from the phosphate anion, a kinetically stable species in the reaction mixture. Perhaps one could imagine reaction conditions with sufficient energy to cleave the P–O bonds, but in most syntheses PO_4^{3-} will remain intact. We can disregard Pb and Cu phases constructed including P, allowing for a reasonable estimation of defect formation energies.

The problem is more complex for molecules containing protons. For example, in formamidinium lead triiodide, interstitial

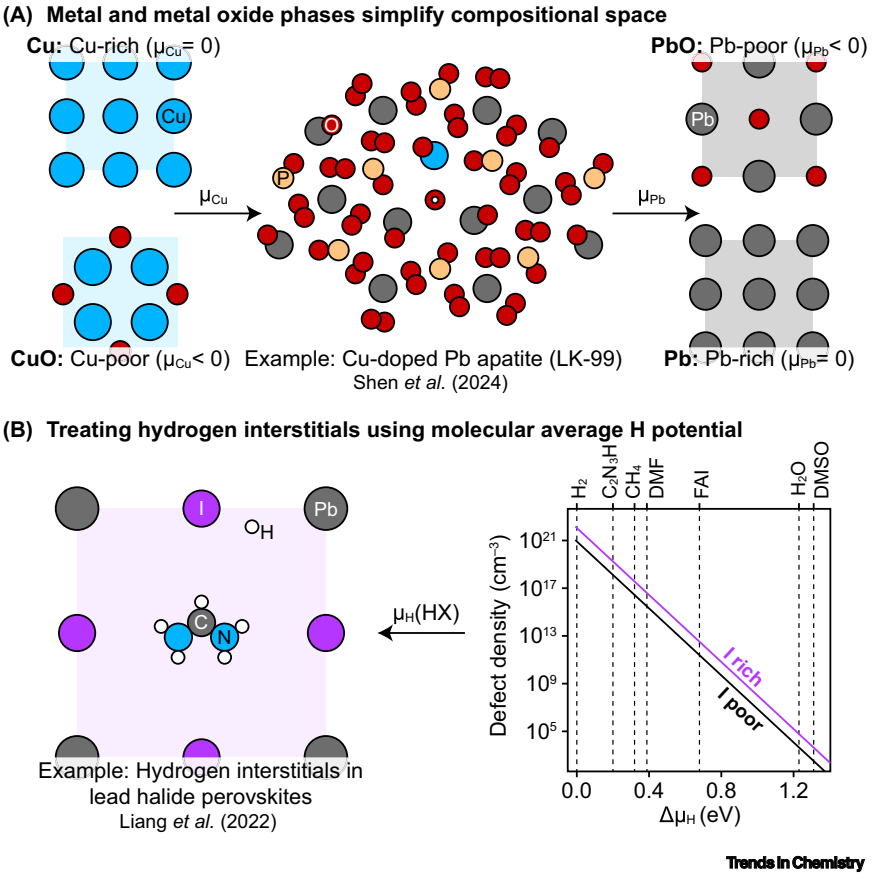

Figure 1. Chemical potentials are phases that provide and extract atoms to and from defective materials. (A) Cu interstitials in Pb apatite may be computed as phase competing to extract Cu atom from bulk Cu (rich potentials) or other phases (e.g., CuO; poor). This substitution necessitates the addition of a Pb atom to either bulk Pb (rich) or other phases (e.g., PbO; poor). (B) The same technique can be applied to interstitial hydrogen in formamidinium lead triiodide, where μ_H maps to the potential of H atoms in the molecular H-sources. This is challenging for molecules like dimethylformamide (DMF) which have two distinct H environments. See [3,4].

hydrogen is predicted to form in substoichiometric concentrations depending on the source of $H^{+/\bullet/-}$, Figure 1B [4]. However, the chemical potential for interstitial hydrogen atoms (μ_H) inherently assumes that all hydrogens in the phase-competing donor molecule are chemically equivalent. This is true for water, methane, and dimethylsulfoxide, but certainly not true for dimethylformamide. Extraction of a single H atom yields an unstable molecule – $C_3N_2H_6^{+/\bullet/-}$ – which is neither kinetically nor thermodynamically stable.

Since molecules often have H atoms in different chemical environments, one must consider which protons are the most labile [5]. One strategy to overcome this is to create a complete balanced chemical reaction. For example, one could compute the formation energy of a charge neutral H-interstitial in formamidinium lead triiodide by the stepwise removal of two H atoms from formamidine to form cyanamide, a highly reactive but kinetically stable molecule. There, the first and second hydrogen atom removals occur at different potentials, but what becomes of both singly and doubly dehydrogenated H_2O [6] in cases where water is the source of H? In the case of interstitial hydrogen inclusion, the molecular species that relinquished the hydrogen atom has been stoichiometrically dehydrogenated and is chemically dissimilar to extracting a Cu atom from an infinitely large portion of CuO.

Correctional terms for highly localized systems

There are different approaches to treat the background potential installed by a charged defect, with some approaches working better for systems with symmetric, delocalized electrostatic potential [7]. One of the more prevalent schemes proposed by Freysoldt *et al.* [8] models the defect charge density isotropically as Gaussian and aligns the distribution to the periodic boundary conditions of the defect (see Figure 2A). While the approach is widely used and readily adapted to a wide range of systems such as rare-earth defects in ZnS [9], the approach may struggle for defects that involve local dipoles and anisotropic bonding. More modern schemes that account for local anisotropy may be better suited for studying defects in molecular materials.

Kumagai and Oba [10] proposed an anisotropic atomic site potential scheme, Figure 2B. This approach modifies the Freysoldt, Neugebauer, and Van de Walle (FNV) scheme to include directional dependence in the dielectric screening, as well as the potential alignment. By using site-dependent potentials this scheme can screen the Gaussian charge distribution to better capture the local environment around the defect and has been applied to anisotropic van der Waals structures (e.g., Sb_2Se_3 [11]) and others.

More recently, other techniques have been introduced that calculate the correctional term from the self-consistent charge density and potential [12,13]. Both the charge density and potential schemes have been used to study a variety of solid-state defects [14], although not yet applied to molecule-containing materials (Figure 2C). Other approaches have been applied to molecular materials [15] and offer some

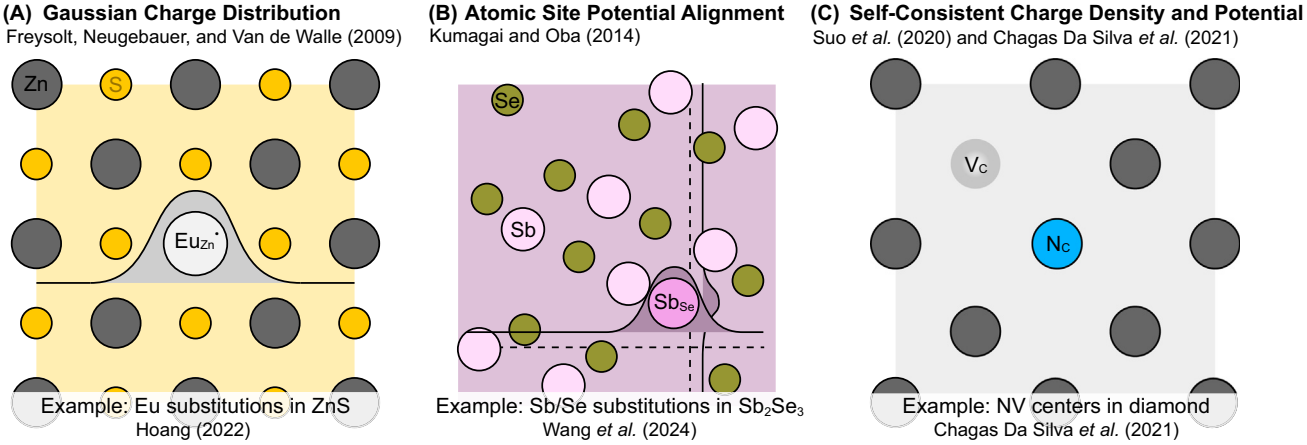

Figure 2. Correcting for charged defects using isotropic and anisotropic sampling methods. (A) In the Freysoldt, Neugebauer, and Van de Walle (FNV) scheme, the defect charge density is modeled as an isotropic Gaussian. (B) Kumagai and Oba use atomic site potentials to screen the Gaussian charge density anisotropically and calculate the alignment from an average. (C) The correction term can also be computed from the self-consistent charge and potential. See [8–13].

advantages and limitation depending on the property of interest. For example, certain density functional theory (DFT) functionals tend to recover accurate defect electronic energy levels in systems where the defect wave functions mix with the bulk material wave functions (i.e., a higher degree of covalency).

Treating substitutions, interstitials, and vacancies in molecular materials

Generally, molecules have dipoles and defects result in a decrease in the host material's rotational symmetry, leading to anisotropic electron density. Thus, the ideal correctional scheme should account for the local fields created by the defect near the molecule. Because of this, correctional terms that implicitly account for dissimilar charge density are well-suited to studying such defects, and the schemes of Kumagai and Oba, and Suo *et al.*, are suitable options. Complementarily, a thorough treatment of μ_i is one that accounts for the product of the chemical reaction involving molecules. Without this the energetics of defect formation may be non-physical. A judicious selection of competing molecular phases and their reaction products will yield good energy predictions.

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Declaration of interests

The authors have no interests to declare.

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