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Toward Modeling Charge-Defect Reactions at the Atomistic Level

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ABSTRACT

Defect reactions involving charged species are commonplace in nuclear fuels fabrication and burn-up. Even the simplest of these fuels, uranium dioxide (UO_2), typically involves the nominal charge states of +3, +4, and +5 or +6 in U and -1 and -2 states in O. Simulations that attempt to model evolutionary processes in the fuels require tracking changes among these charge states.

At the atomistic level, modeling defect reactions poses a particularly vexing problem. Typical potential energy surfaces do not have this type of physical phenomena built into them. Those models that do attempt to model charge-defect reactions do not have especially strong physical bases for the models. For instance, most do not obey established limits of charge behavior at dissociation or lack internal consistency.

This work presents substantial generalizations to earlier work of Perdew *et al.* No matter the size of the system, total system hamiltonians can be decomposed into subsystem or site hamiltonians and coulombic interactions. Site hamiltonians can be evaluated in a spectral representation, once an integer number of electrons are assigned. For both pair and individual site hamiltonians a dilemma emerges in that many sites are better understood as possessing a fractional charge. The dilemma is how to weight the site integer-charge states in a physically consistent manner.

One approach to solving the dilemma results in two distinct charge-dependent energy contributions emerge, arising from intra- and inter-subsystem charge transfer. Further analysis results in a model of the intra-subsystem charge-transfer that can accommodate the mixed valence states of either U or O in nuclear fuels. Mixed valence properties add complications to the model that originate in the phenomenological fact that it typically requires different amounts of energy to increase or decrease charge. As a result of the inherent complexity one has the option of using multiple charges, a concept with strong ties to shell models, or modeling parameters not directly related to charge as functions of charge. This later approach is illustrated by invoking a minimization principle that does preserve the important dissociation limits of Perdew *et al.*, in order to complete the model.

INTRODUCTION

Numerous materials applications depend on transformations of the electronic structure in the material. Among the most important of these entail transitions between metallic and insulators or among different grades of metals. Examples of importance of such transformations include actinide alloys (e.g. U_6Nb and Ga-stabilized Pu), superconductor-semiconductor-metal transitions (e.g. YBCOs) and thermally-driven transformations on metal oxides (e.g. VO_2). Similarly defects can produce local electronic changes such as changes of valence. For example, deviations in oxygen stoichiometry from the UO_2 line compound can induce generation of U^{+3} , U^{+6} , and O^{-1} species. Substitution of Pu for U can induce charge reactions. Fission damage undoubtedly entails large numbers of ionic defect production and annihilation reactions.

We begin our query about such events by looking at electron localization more generally. At one extreme, good metals show extensive, uniform delocalization of their valence electrons. Correlations among electrons are considered weak and the local density approximation (LDA) [1] is generally considered to be an adequate model. “Bad” metals, semiconductors and insulators exhibit varying degrees of localization of their electrons. Such localization is considered strong electron correlation. To model such materials, elements of the Hubbard model [2] are added to LDA (LDA+U) [3]. The Hubbard model introduces a rudimentary form of localization. The parameter U from this model modulates the amount of localization, and the transition from metallic to insulating behavior (Fig. 1) can vary continuously. Its value is related to electron-electron repulsion from electrons being added or subtracted from an atom in a

Figure 1. The variable ν is a quantum mechanical mixing parameter to describe the Hubbard model. The value of U , the average electron-electron repulsion, controls the level of localization in the model. Details are described below.

material. Much more rigorous first-principles theories of strong electron correlation have recently captured the martensitic phase transformation in Pu (DMFT – [4,5]) and calculated the band gap in UO_2 (“hybrid” density functional theory (DFT) – [6]).

Here we examine implications of Hubbard-type thinking for the charge dependence of the energy on an atom in contact with a fluctuating electron medium. We do this by looking directly at the variational energy of a three state model. The eventual application of the resulting model is intended to be atomistic level models of charge dependencies that can model materials undergoing electronic phase transformations and ionic reactions. The usual level of atomistic model can be summarized from the Buckingham potential and atomic terms related to ionization processes or change of valence. For atom X in contact with environment Y, the atomistic energy expression is taken to be

$$E = (\mu_X - \mu_Y)q + \frac{1}{2}(\eta_X + \eta_Y)q^2 + A \exp(-R/R_0) - C/R^6 - q^2/R, \quad (1)$$

where μ_X and μ_Y are chemical potentials or Fermi energies, η_X and η_Y are hardnesses or band gaps, q is the charge on X, C is a dispersion coefficient, R is a bond length or neighbor distance, and R_0 and A are constants determining short-range interactions. See for example the ES+ [7], ReaxFF [8], and BKS [9] models. Direct optimization of E with respect to q yields

$$q = -\frac{\mu_X - \mu_Y}{\eta_X + \eta_Y - 2/R}, \quad (2)$$

This model of q goes to a non-zero value at large R , a physically incorrect result [10]. ReaxFF [8], and BKS [9] models empirically correct this deficiency. The intent here is to develop a first-principles view of correct asymptotic form that also connects to the broader concepts of strong electron correlations and charge fluctuations.

THEORETICAL CONCEPTS

Electronic structure methods such as Hubbard models [2,3], DMFT [4,5] and hybrid DFT [6] seek to capture strong electron correlations effects beyond what can be attained through LDA-level theories. In the simplest terms these methods introduce quantum charge fluctuation states. We focus on the Hubbard model because it is the simplest of these. Three states are permitted for each site: 1 mean-field state (degenerate $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$) and two charge-fluctuation states, $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$. The mean field-state is responsible for metallic behavior and the state is delocalized. The charge-fluctuation states are responsible for insulating properties and are localized. For our purposes then, the Hubbard energy can be rendered as [11]

$$E_{\text{Hubbard}} \sim E_0 + 2tv\sqrt{(1-v^2)} + Uv^2(1-v^2), \quad (3)$$

where $t < 0$ and U are traditional Hubbard hopping integral and average electron-electron repulsion energies, respectively. The mixing parameter v varies between 0 and 1 (Fig. 1).

To connect the Hubbard model with more general origins and with charges, we write an arbitrary variational energy in the spectral form [12]

$$\langle \psi | H | \psi \rangle = \sum_K |\langle \psi | \Psi_K \rangle|^2 E_K \equiv \sum_K \omega_K E_K, \quad (4)$$

where H is the system hamiltonian and ψ is an arbitrary trial state. The eigenstates are the Ψ_K with energies E_K . The ω_K are the occupation numbers defined as the squares of the overlaps.

For the 3-state model implied by Hubbard, the unnormalized, mixed state of the system $\psi = |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle + \Gamma |\downarrow\downarrow\rangle + \Lambda |\uparrow\uparrow\rangle$, where Γ and Λ are mixing coefficients for the charge fluctuation or ionic states. The values of Γ are unrestricted while those of Λ are confined to the interval $[-1, 1]$. In general, none of the three Hubbard states is an eigenstate. Thus the contributing energies come from mixing all three states. It is only at large separations, when even good metals go through a Mott transition and their bands become very narrow that the Hubbard states become eigenstates [2]. Then the variational energy becomes

$$\bar{E}(q, \Lambda) = E_0 + \omega_1(q, \Lambda)(E_1 - E_0) + \omega_2(q, \Lambda)(E_2 - E_0) . \quad (5)$$

The charge $q = (\Gamma^2 - \Lambda^2)/(1 + \Gamma^2)$ has been substituted in place of Γ as discussed in Ref. 13. It is also confined to the interval $[-1, 1]$. When the states do not overlap significantly, as assumed by Hubbard and many others, we can write the occupation numbers analytically in the form

$$\begin{aligned} \omega_K(q, \Lambda) &= \frac{\left(\sqrt{(1 - \Lambda^2)(1 - \Lambda_K^2)} + \Lambda \Lambda_K + \Gamma \Gamma_K \right)^2}{(1 + \Gamma^2)(1 + \Gamma_K^2)} \\ &= \frac{\left(\left[\sqrt{(1 - \Lambda^2)(1 - \Lambda_K^2)} + \Lambda \Lambda_K \right] \sqrt{(1 - q)(1 - q_K)} \pm \sqrt{(q + \Lambda^2)(q_K + \Lambda_K^2)} \right)^2}{(1 + \Lambda^2)(1 + \Lambda_K^2)} , \end{aligned} \quad (6)$$

where q_K , Γ_K and Λ_K are eigen-charges and mixing coefficients. Note that introducing the charge has produced a branch in the total variational energy surface. The ground state is in the branch with the minus sign in Eq. 6. The variational energy for an OH molecule calculated from the VB2000 electronic structure code is shown in Fig. 2 [14].

In general Λ acts like an environmental variable that changes the energy dependence accordingly. These results are telling us that equivalent q dependencies in Eq. 1 should vary with environment. The parabolic line in Fig. 2, representing the traditional electrostatic dependence, overlays the current results to increase the contrast.

Figure 2. Charge dependence of the variational energy is calculated from Eq. 4 for a fixed bond length of the OH molecule. The variational energy is also a function of the environmental

variable Λ . Optimizing Λ as a function of q produces a slice through this surface with a character similar to the Hubbard variational energy, Eq. 2.

The final step needed to get to an expression that resembles Eq. 2 is to make Λ a function of q . One can achieve this relationship through a partial optimization [13]. This optimization can be expressed as

$$\bar{E}(q) = \min_{-1 \leq \Lambda \leq 1} \bar{E}(q, \Lambda) = \bar{E}(q, \Lambda_{\text{opt}}(q)) . \quad (7)$$

The outcome of the optimization creates a cut through Fig. 2 that resembles the curves in Fig. 1. In general, this is a polynomial dependence, as suggested by the Hubbard energy. However, the detailed shape of Fig. 2 changes with the strength of the interaction. Such shape changes can result in very sharp corners in the surface that are related to jumps in chemical potential [2,10,12]. In such cases, the optimization in Eq. 7 cannot be achieved by taking the derivative of Eq. 5 with respect to q . Otherwise, one arrives again at the unphysical behavior of Eq. (2).

To model ions like U in nonstoichiometric $\text{UO}_{2\pm x}$ that can be in several valence states that are not centered around 0, one needs to slightly modify the present expressions. First, q is replaced by $q - Z_0$ in the occupation numbers, where Z_0 is an interior value of the valence. Second the relationship between q and the mixing coefficients must be replaced with $q - Z_0 = ((Z_+ - Z_0) \Gamma^2 + (Z_- - Z_0) \Lambda^2) / (1 + \Gamma^2)$, where Z_+ and Z_- are the upper and lower values of the possible valence states, respectively. Thus one is able to represent a situation where U could take on +3 (Z_-), +4 (Z_0) and +6 (Z_+) states, for instance, as suggested by some experiments and first principles calculations. All values of q within this range are permitted as well.

CONCLUSIONS

The present analysis extends traditional thinking about charge dependencies of energies by constructing variational energies as functions of charge. This approach suggests new principled alternatives to traditional electrostatic atomistic models of charge dependence. At the same time, they provide an avenue for connecting to Hubbard models. Such developments are need for atomistic methods to correctly capture high quality, first-principles and experimental information for use in advanced simulations.

Like the Hubbard model there are two energy scales given by the two gap energies. The physical interpretation is slightly different, but this is mostly due to the more qualitative nature of the Hubbard model. Here we have not made any approximation about the value of the electron-electron repulsion on a site. We have only used the ideas that (1) the variational energy can be expanded in a spectral representation and (2) the charge can be made an explicit function of the mixing parameters in the wavefunction. Nevertheless, the availability of the two energy scales, in concert with environmental variable Λ , yields the flexibility needed for mixed and changing valence.

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