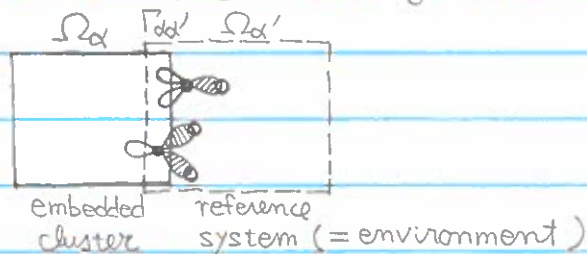


Embedded-Cluster Boundary Condition: Orbital Approach

7/9/03

— Frozen orbital

[N. Reuter, A. Dejaegere, B. Maigret, M. Karplus, JPC A 104, 1720 ('00)]



1. Solve the electronic-structure problem in the reference system, which accurately describes the cluster boundary.

$$H\phi_n^{(\alpha')} = \epsilon_n^{(\alpha')} \phi_n^{(\alpha')}$$

2. Project the eigenstates to the (sp^3) bonds, w_μ , directing away from the cluster. (Requires chemistry knowledge.)

Calculate the occupation of w_μ as

$$\begin{aligned} & \langle w_\mu | P | w_\mu \rangle \\ = & \langle w_\mu | P | w_\mu \rangle \quad (\oplus - P^2 = P) \end{aligned}$$

$$= \sum_n \langle w_\mu | n \rangle \theta(\mu - \epsilon_n) \langle n | w_\mu \rangle$$

$$= \sum_n |\langle w_\mu | n \rangle|^2 \theta(\mu - \epsilon_n) \equiv P_\mu \quad (1)$$

The edge Wannier orbital w_μ is frozen with amplitude $\sqrt{P_\mu}$ to compute $v_{\text{eff}}(r)$. (In the divide-d-conquer scheme, in which v_{eff} is computed globally with $\rho(r) = \sum_\alpha \rho_\alpha(r)$, the fractional occupation is irrelevant.)

3. Orthogonalize the basis in Ω_α to $\{w_\mu \in \Gamma^{\alpha\alpha'} = \Omega_\alpha \cap \Omega_{\alpha'}\}$.

Embedded Cluster: Environmental MO's

(2)

[H.A. Duarte & D.R. Salahub, JCP 108, 743 (1988)]

1. Solve the reference electronic-structure problem; perform unitary transformation to obtain maximally localized Wannier functions $\{\psi_\mu\}$, which are occupied,

$$|\psi_\mu\rangle = \sum_n |\phi_n^{(\alpha)}\rangle U_{n\mu} \quad (2)$$

(Use Boys' method to minimize packet-spread or maximize dipole moment.)

2. Freeze the environment orbitals by modifying Hamiltonian

$$\tilde{H} = H + \sum_{\mu\nu}^{\text{env}} \sum_n^{\text{Wannier eigen}} |\mu\rangle \langle \mu | n^{\alpha'} \rangle (-2\varepsilon_n^{(\alpha')}) \langle n^{\alpha'} | \nu \rangle \langle \nu | \quad (3)$$

* "...we are just assuring that the cluster MO's will remain orthogonal to the environmental MO's." ?

1 Note

$$\begin{aligned} P &= \sum_n^{\Omega_{\alpha'}} |n^{\alpha'}\rangle (-2\varepsilon_n^{(\alpha')}) \langle n^{\alpha'}| \\ &= 2 \sum_n^{\Omega_{\alpha'}} |n^{\alpha'}\rangle (E - \varepsilon_n^{(\alpha')}) \langle n^{\alpha'}| \Big|_{E=0} \\ &= G^{-1}(E) \Big|_{E=0} \end{aligned} \quad (4)$$

First-Order Perturbation & Reference System ③

[O.F. Sankey & D.J. Niklewski, PRB 40, 3979 ('89)]

cf. J. Harris, PRB 31, 1770 ('85)

- First-order perturbation DFT

1. Start with a reference density $\rho_{\text{ref}}(r)$; e.g.,

$$\rho_{\text{ref}}(r) = \sum_l \rho_{\text{atom}}^{(l)}(r - R_l) \quad (1)$$

2. Solve KS equations only once with $v_{\text{eff}}[\rho_{\text{ref}}(r)]$

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}[\rho_{\text{ref}}(r)] \right) \psi_n(r) = \epsilon_n \psi_n(r) \quad (2)$$

3. First-order perturbative density is

$$\rho(r) = \sum_n \theta(\mu - \epsilon_n) |\psi_n(r)|^2 = \rho_{\text{ref}}(r) + \delta\rho(r) \quad (3)$$

* $\delta\rho(r)$ contains first-order approximation to covalent bond formation.

* Use $\rho_{\alpha'}(r)$ in the divide-&-conquer for "first-order approximation" to $\Omega_{\alpha} - \Omega_{\alpha'}$ covalent bonding, instead of rigid-wall termination of Ω_{α} and $\Omega_{\alpha'}$.

- Linear combination of pseudo-atomic orbitals (LSPO)

Solve unscreened pseudoatom problems with short-range constraint

$$R_l^{\text{PAO}}(r) \Big|_{r=r_c} = 0 \quad (4)$$