Multiscale Schemes for the Predictive Description and Engineering of Materials

Sandia National Laboratories

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Problem

Materials Design from Scratch — Why?

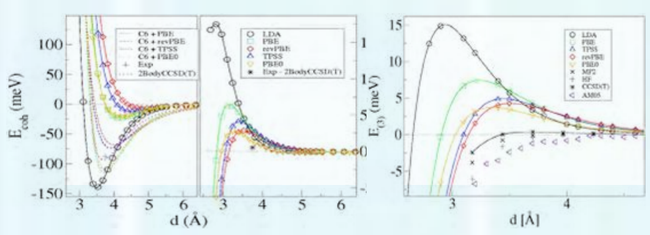
Herringbone (300 K) and hexagonal (400 K) configurations of C_{132}; columnar disordered (400 K) of $C_{10\cdots6}$

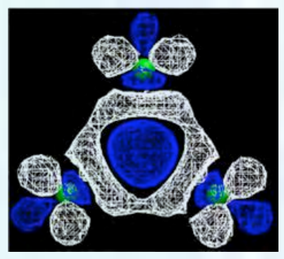
Approach

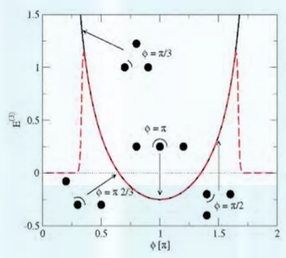
- Multiscaling to link microscopic to macroscopic properties: QM/QM/MM/MM/CG/CM ...
- Sufficient Accuracy: van-der-Waals in DFT
- Exploring Chemical Compound Space (CCS):
  - Molecular grand-canonical ensemble DFT
  - Alchemical potential in CCS
  - Transmutational gradients in CCS
- Optimization Algorithms in CCS

Results

vdW & DFT







$$E^{(3)}_{IJK} = C9_{IJK}\frac{3\cos[\phi_\alpha]\cos[\phi_\beta]\cos[\phi_\gamma]+1}{R^3_{IJ}R^3_{IK}R^3_{JK}}$$

$$C6_{IJK} = \frac{3}{\pi}\int_0^\infty d\omega\,\alpha_I(i\omega)\alpha_J(i\omega),$$

$$C9_{IJK} = \frac{3}{\pi}\int_0^\infty d\omega\,\alpha_I(i\omega)\alpha_J(i\omega)\alpha_K(i\omega)$$

$$C9_{IJK} \approx \frac{8}{3}\frac{P_IP_JP_K(P_I+P_J+P_K)}{(P_I+P_J)(P_J+P_K)(P_K+P_I)},$$

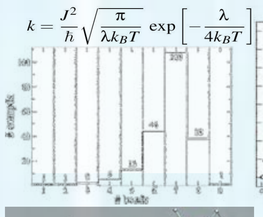
$$P_I = C9_{III}\frac{\alpha_{0_J}\alpha_{0_I}}{\alpha^2_{0_I}}$$

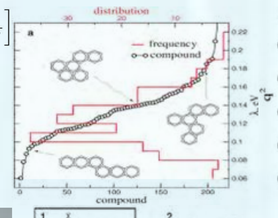
$$C9_{III} \approx \left(\frac{V_I}{V_I^{free}}\right)^3 C9^{free}_{III}$$

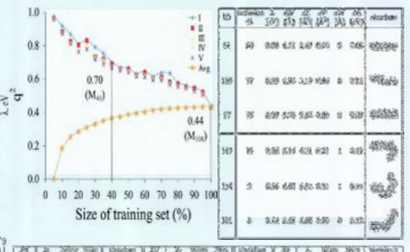
With Alexandre Tkatchenko (Fritz-Haber-Institute)

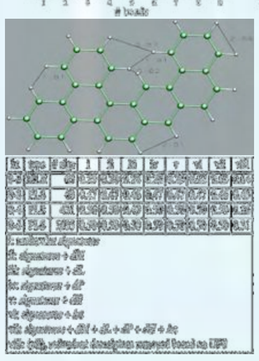
QSPRs for PAH

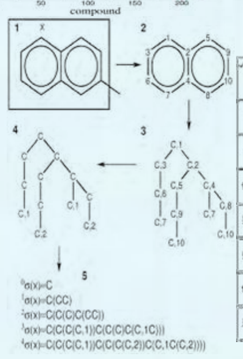
$$k = \frac{J^2}{\hbar}\sqrt{\frac{\pi}{\lambda k_BT}}\exp\left[-\frac{\lambda}{4k_BT}\right]$$









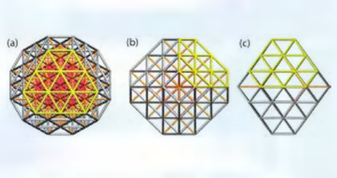


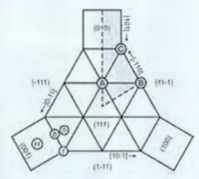
With Milind Misra (SNL), Denis Andrienko (Max-Planck Institute), Jean-Loup Faulon (Paris)

Results (cont.)

Nano-cluster core-shell catalysts

$$E_a^{CH_3+H} = E(CH_3+H+Pd@Pd) - E(CH_3) - E(H) - E(Pd@Pd)$$





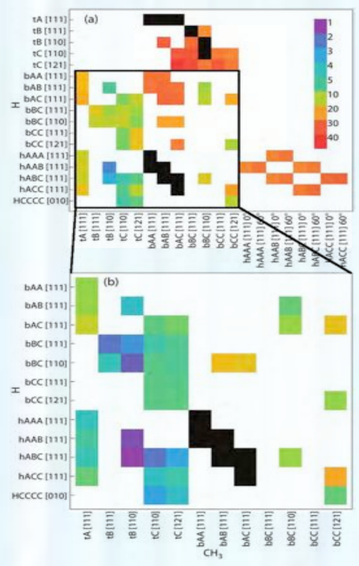


TABLE III: Methane Dissociative Adsorption Energy Relative to X@Pd + CH_3 + H [kcal/mol]

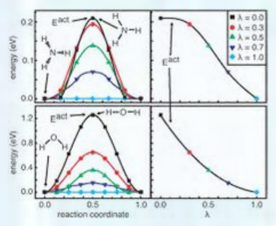
Site	Fixed Cluster Pd@Pd	Fixed Cluster Cu@Pd	Fixed Cluster Cu@Pd[‡]	Fixed Core Pd@Pd	Fixed Core Cu@Pd	Fixed Core Cu@Pd[§]
tB [110]/ hABC [111][†]	-102.5	-96.9	-5.3	-104.4	-101.5	3.6
hBC [110]/ hBC [110][†]	6.9	5.9	7.1	6.8	6.3	6.4
tB [110]/ bBC [110][†]	-95.6	-91.0	12.4	-97.6	-95.2	10.0
tA [111]/ hAAA [111]	-94.7	-85.8	12.1	-102.0	-95.0	7.9

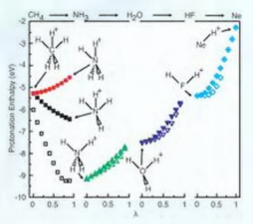
[‡] Geometry taken from Pd@Pd. [†] CH_3 constrained to remain over Pd atom. [§] Relaxed geometry from Pd@Pd tB [110]/ bBC [110] without CH_3 constraint.

With Robin Hayes (NYU)

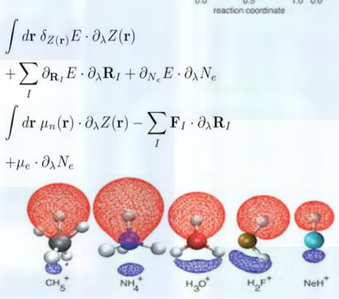
Alchemical changes

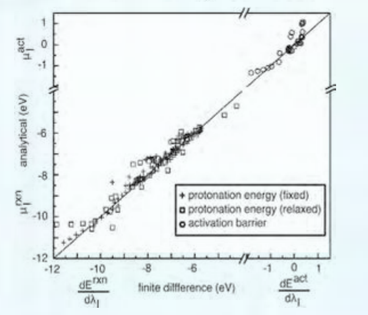
λ=0	λ=1	property
CH_4	NH_3	ΔH
NH_3	H_2O	ΔH, E^{act}
H_2O	HF	ΔH, E^{act}
HF	Ne	ΔH





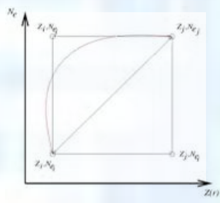
$$\partial_\lambda E = \int d\mathbf{r}\,\delta_{Z(\mathbf{r})}E\cdot\partial_\lambda Z(\mathbf{r}) + \sum_I \partial_{\mathbf{R}_I}E\cdot\partial_\lambda\mathbf{R}_I + \partial_{N_e}E\cdot\partial_\lambda N_e = \int d\mathbf{r}\,\mu_n(\mathbf{r})\cdot\partial_\lambda Z(\mathbf{r}) - \sum_I \mathbf{F}_I\cdot\partial_\lambda\mathbf{R}_I + \mu_e\cdot\partial_\lambda N_e$$





With Dan Sheppard & Graeme Henkelman (UT Austin)

Accurate gradients in CCS



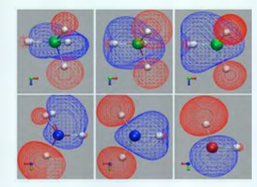
$$\frac{\partial E[H(\lambda,N_e)]}{\partial\lambda} \overset{HF}{=} \left\langle\frac{\partial H(\lambda)}{\partial\lambda}\right\rangle_{\lambda,N_e} = \int d\mathbf{r}\,n_\lambda(\mathbf{r})v_t(\mathbf{r})$$

$$\frac{\partial E(\lambda)}{\partial\lambda} = \int d\mathbf{r}\,n_\lambda(\mathbf{r})\times[v_j(\mathbf{r})-v_i(\mathbf{r})]$$

$$E^L = E_i + \lambda\times(E_j-E_i)$$

$$E[H(\lambda)] = E[H_i + f_{ij}(\lambda)\times(H_j-H_i)]$$

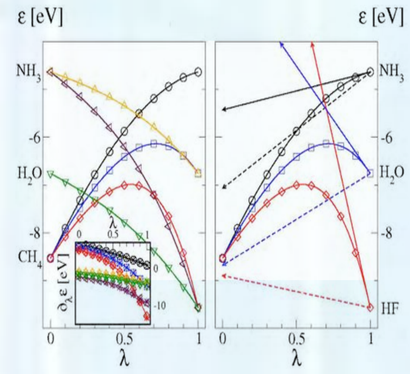
$$f_{ij}(\lambda) = \begin{cases}0 & \leftrightarrow \lambda=0\\ 1 & \leftrightarrow \lambda=1\end{cases}$$



$$H(\lambda) = H_i + (\lambda + a_{ij}\cdot[\lambda^2-\lambda])\times(H_j-H_i).$$

$$\partial_\lambda E^L = E_j - E_i \overset{!}{=} \langle\partial_\lambda H\rangle$$

$$a_{ij} = \left(\frac{E_j-E_i}{\langle H_j-H_i\rangle_\lambda}-1\right)\times\frac{1}{2\lambda-1} = \left(\frac{\partial_\lambda E^L}{\partial_\lambda E(\lambda)}-1\right)\times\frac{1}{2\lambda-1}$$



Predicted cmpd	ϵ_{act}	$a=0$	$a^{(ref\_1)}$	$a^{(ref\_2)}$
CH_4	**-8.54**	$\epsilon_{\leftarrow HF}$ *+4.41*	$a^{ref}_{C_2H_6,CH_3F}$ -8.90	$a^{ref}_{C_3H_8,C_2H_5F}$ -9.01
CH_3-CH_3	**-7.64**	$\epsilon_{\leftarrow CH_3F}$ *+2.15*	$a^{ref}_{CH_4,HF}$ -7.37	$a^{ref}_{C_3H_8,C_2H_5F}$ -7.72
CH_3-CH_2-CH_3	**-7.52**	$\epsilon_{\leftarrow CH_3CH_2F}$ *+0.06*	$a^{ref}_{CH_4,HF}$ -7.25	$a^{ref}_{C_2H_6,CH_3F}$ -7.45

Significance

- Corrected DFT will greatly enhance the predictive quality of ab initio materials simulation
- Sampling the molecular grand-canonical ensemble will render routine optimization of chemical compounds as straightforward as performing ordinary ab initio molecular dynamics
- Multiscale coupling will permit linking the atomistic design of properties to materials' macroscopic behavior
- Compound design will permit the in silico design of materials exhibiting desired properties, relevant to Sandia's mission

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND2009-5185P

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