

# Zero and Finite Temperature Adsorption Energies in Zeolites: A Random Phase Approximation Study

A. Dixit, M. Badawi, T. Bučko, S. Lebègue, J. Ángyán and D. Rocca  
 Université de Lorraine and CNRS, CRM<sup>2</sup> Laboratory, Vandoeuvre-lès-Nancy, France

CRM<sup>2</sup>



Starting from the general expression for the ground state correlation energy in the adiabatic connection fluctuation dissipation theorem (ACFDT) framework, the dielectric matrix formulation is applied to calculate the random phase approximation (RPA) correlation energy. Through the use of a compact auxiliary basis set and the use of density functional perturbation theory (DFPT) techniques, this dielectric matrix-based formalism can be efficiently implemented within a plane-wave basis set framework [1]. The adsorption energies of methane and carbon dioxide on siliceous chabazite are then computed at the RPA level. Convergence tests are shown to determine the stability of our results. By using ten configurations generated by molecular dynamics simulations at the PBE+D2 level at 300 K, adsorption energies for methane on chabazite are computed at the RPA level.

## RPA within ACFDT

Within the adiabatic connection fluctuation dissipation theorem (ACFDT),

$$E_c^{ACFDT} = -\frac{1}{2} \int_0^1 d\alpha \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{Tr} \{ \chi_\alpha(i\omega) \mathbf{K} - \chi_0(i\omega) \mathbf{K} \}$$

$$K_{vc,v'c'} = 2 \langle v, c' | V | c, v' \rangle$$

Random Phase Approximation (RPA) for  $\chi_\alpha$ :

$$\chi_\alpha = (\mathbf{I} - \alpha \chi_0(i\omega) \mathbf{K})^{-1} \chi_0(i\omega)$$

$$E_c^{RPA} = \frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{Tr} \{ \log(\mathbf{I} - \chi_0(i\omega) \mathbf{K}) + \chi_0(i\omega) \mathbf{K} \}$$

- In case of solids,

$$K_{vc,v'c'}(\mathbf{q}) = 2 \int \phi_v^{\mathbf{k}}(\mathbf{r}) \phi_c^{\mathbf{k}+\mathbf{q}*}(\mathbf{r}) V(\mathbf{r}, \mathbf{r}') \phi_{c'}^{\mathbf{k}+\mathbf{q}}(\mathbf{r}') \phi_{v'}^{\mathbf{k}*}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$$E_c^{RPA} = \frac{1}{2} \frac{1}{N_q} \sum_{\mathbf{q}} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{Tr} [ \log \{ \mathbf{I} - \chi_0(\mathbf{q}, i\omega) \mathbf{K}(\mathbf{q}) \} + \chi_0(\mathbf{q}, i\omega) \mathbf{K}(\mathbf{q}) ]$$

## Numerical Implementation for Plane-Waves

The large size of a plane-wave basis set requires the use of a compact auxiliary basis set to represent  $\chi_0$ .

$$\chi_0^{mn} = \int U_m(\mathbf{r}) \chi_0(\mathbf{r}, \mathbf{r}') U_n(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$$= 4 \text{Re} \sum_{cv} \frac{\langle \phi_v | U_m | \phi_c \rangle \langle \phi_c | U_n | \phi_v \rangle}{\epsilon_v - \epsilon_c}$$

To build this basis set, it is necessary to:

- Remove the linear dependence of the products  $\phi_v(\mathbf{r}) \phi_c(\mathbf{r})$
- Correctly consider the weights  $(\epsilon_v - \epsilon_c)^{-1}$ .

For example: Major contributions from

$$\phi_{\text{HOMO}}(\mathbf{r}) \phi_{\text{LUMO}}(\mathbf{r}), \text{ due to } (\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}})^{-1}$$

Minor contributions from

$$\phi_{\text{HOMO}}(\mathbf{r}) \phi_{\text{LUMO}+50000}(\mathbf{r}), \text{ due to } (\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}+50000})^{-1} \approx 0$$

Based on these observations, the optimal basis set can be constructed by iterative diagonalization of  $\chi_0$  containing the kinetic energy term only:

$$\chi_0 U_m = \int \chi_0(\mathbf{r}, \mathbf{r}', i\omega) U_m(\mathbf{r}') d\mathbf{r}'$$

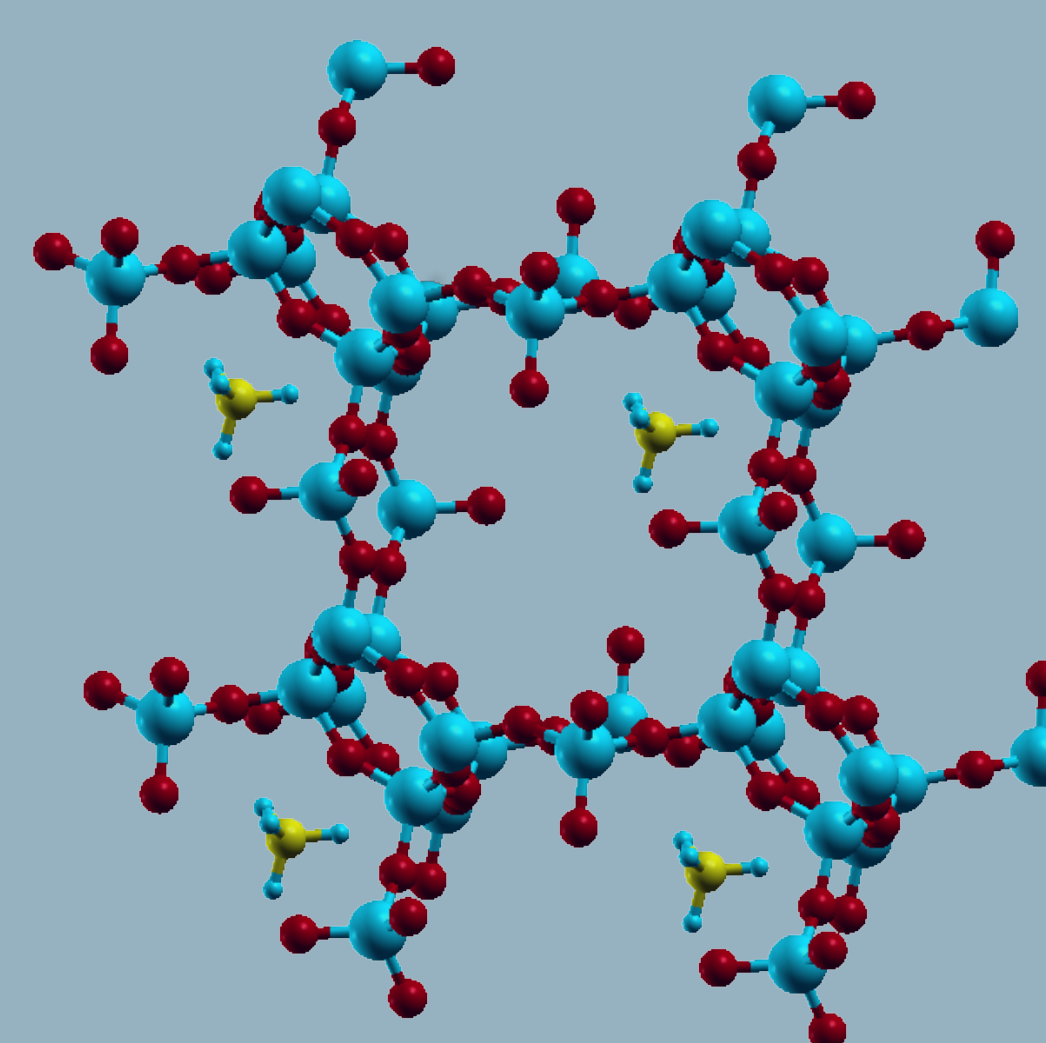
$$= 4 \text{Re} \sum_{cv} \frac{\phi_v^*(\mathbf{r}) \phi_c(\mathbf{r}) \langle \phi_c | U_m | \phi_v \rangle}{\epsilon_v - \epsilon_c}$$

$$= 4 \text{Re} \sum_v \phi_v^*(\mathbf{r}) \hat{Q}(\mathbf{r}) (\epsilon_v - \hat{H})^{-1} \hat{Q}(\mathbf{r}) | U_m \phi_v \rangle$$

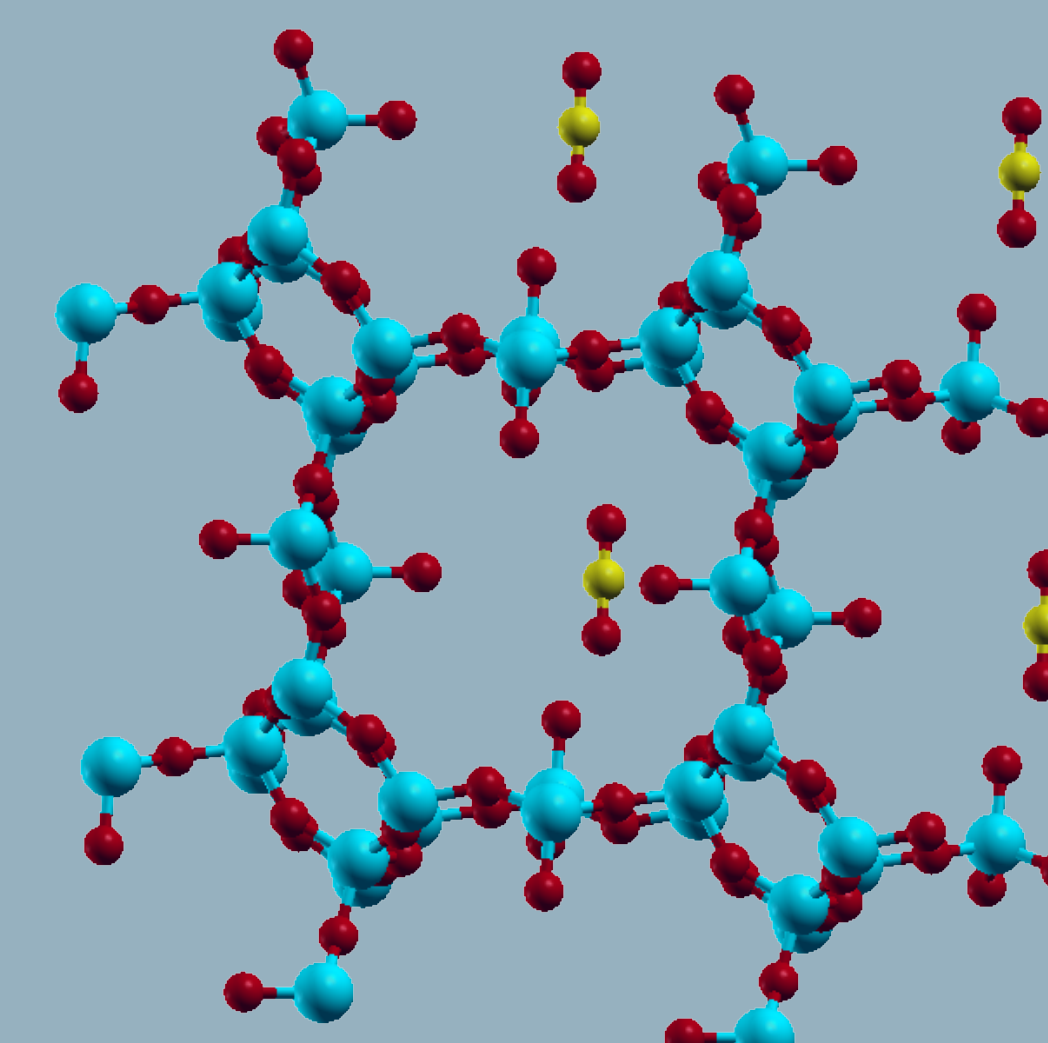
$$\approx 4 \text{Re} \sum_v \phi_v^*(\mathbf{r}) \hat{Q}(\mathbf{r}) \left( \epsilon_v + \frac{\nabla^2}{2} \right)^{-1} \hat{Q}(\mathbf{r}) | U_m \phi_v \rangle$$

- Kinetic energy is a good approximation for the high energy states, and reduces their importance in the basis set generation.
- In addition, the kinetic energy is diagonal in  $\mathbf{G}$ -space and it is trivial to compute its inverse.
- The projector can be expressed as  $\hat{Q} = \sum_c |\phi_c\rangle \langle \phi_c| = 1 - \sum_v |\phi_v\rangle \langle \phi_v|$  and does not need the explicit calculation of unoccupied states.
- This representation removes the linear dependence of the occupied-unoccupied products.
- Once the basis set is generated, it can be used to compute exactly  $\chi_0$  by using the Lanczos algorithm.

## Zeolites



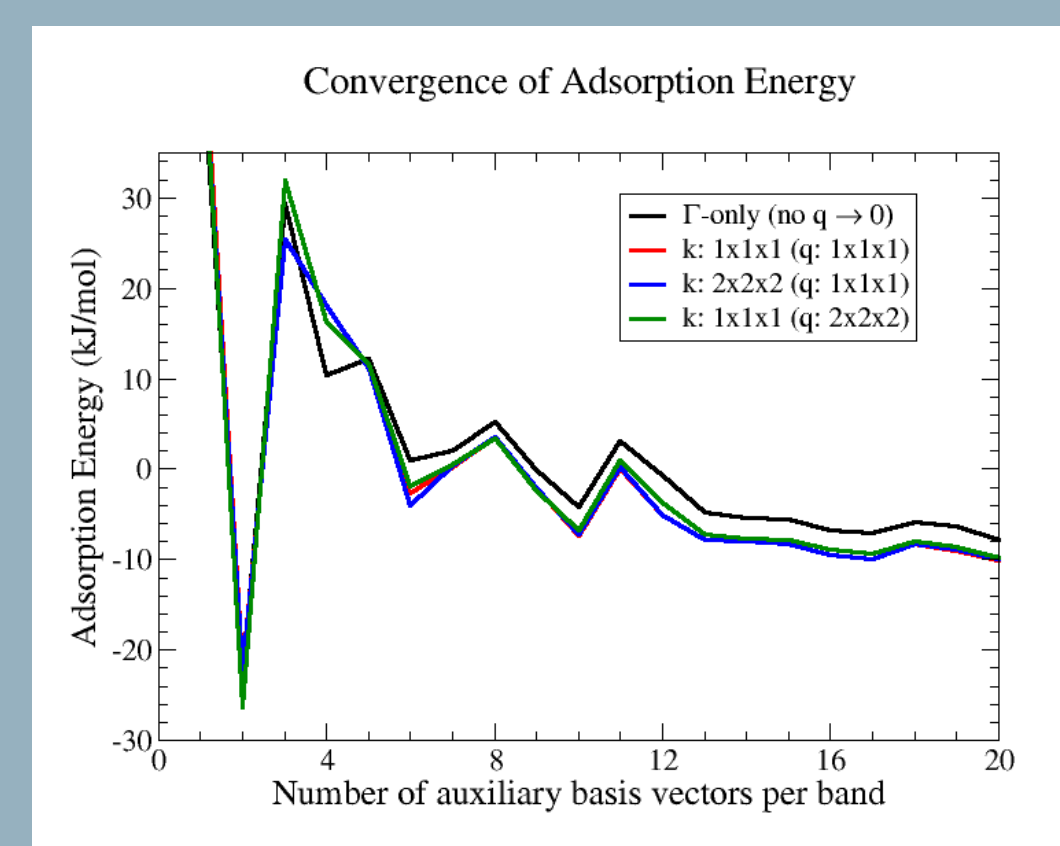
CH<sub>4</sub> adsorption in chabazite



CO<sub>2</sub> adsorption in chabazite

- Zeolites are aluminosilicate compounds with a porous structure.
- Possible to trap different molecules in these pores.
- Tunable characteristics → multiple uses.

## Adsorption in Zeolites



Interaction energies in chabazite (kJ/mol)

Molecule	PBE	RPA ( $\Gamma$ -only)
CH <sub>4</sub>	+1.60	-10.99
CO <sub>2</sub>	-1.36	-18.17

- Methane – Good agreement with earlier calculations[2]
- Carbon dioxide – RPA underestimates experimental values of 24 and 22.5 kJ/mol (300 K)[3, 4]

Convergence of the adsorption energy as a function of the auxiliary basis set for different samplings of  $\mathbf{k}$ - and  $\mathbf{q}$ -points.

## Temperature Effects

- To compare with ‘reality’, it is vital to include temperature effects.
- Average over configurations generated by temperature-dependent molecular dynamics.
- 10 configurations for methane generated by molecular dynamics at 300 K – adsorption energy = **8.4** kJ/mol.
- Ongoing calculations for convergence tests with respect to configurations.

## Future Work

- Adsorption of other molecules – comparison with experiment, acidity, ...
- RPA interaction energies for more configurations obtained from temperature-dependent molecular dynamics simulations.

## Further Reading

- [1] F. Kaoui and D. Rocca. *J. Phys.: Condens. Matt.*, 28:035201, 2016.
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- [3] T. D. Pham, M. R. Hudson, C. M. Brown, and R. F. Lobo. *ChemSusChem*, 7:3031, 2014.
- [4] H. Fang, P. Kamakoti, J. Zang, S. Cundy, C. Paur, P. I. Ravikovitch, and D. S. Sholl. *J. Phys. Chem. C*, 116:10692, 2012.

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