Nissan Leaf

Electrified electrode-electrolyte interfaces from first principles

Arihant Bhandari, Chao Peng, Jacek Dziedzic, Lucian Anton, John R. Owen, Denis Kramer, Chris-Kriton Skylaris

University of Southampton, United Kingdom

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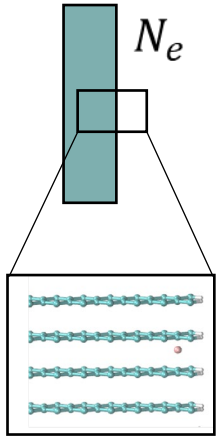
MULTI-SCALE MODELLING

Modelling

Model for simulations of electrified electrode-electrolyte interfaces in ONETEP

Canonical ensemble of electrons
(constant number of electrons)



Atomistic electrode

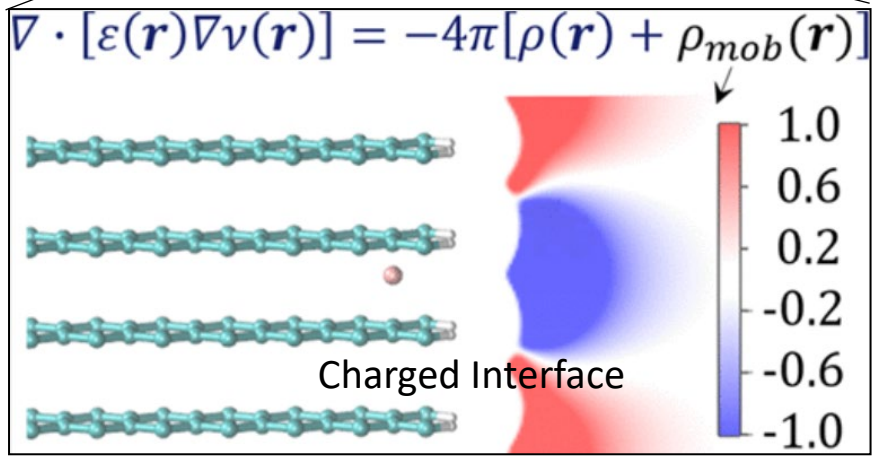
Vacuum

Grand canonical model for electrochemistry

Applied voltage

$\mu_e = \mu_e^{ref} - e \cdot U$

μ_e^{ref}



Atomistic electrode

Continuum solvent and electrolyte

System	μ_e^{ref}, physical scale (eV)
Electron in vac.	0.0
Li^+/Li	−1.39
H^+/H_2 (SHE)	−4.44

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The Journal of Chemical Physics

Electrochemistry from first-principles in the grand canonical ensemble

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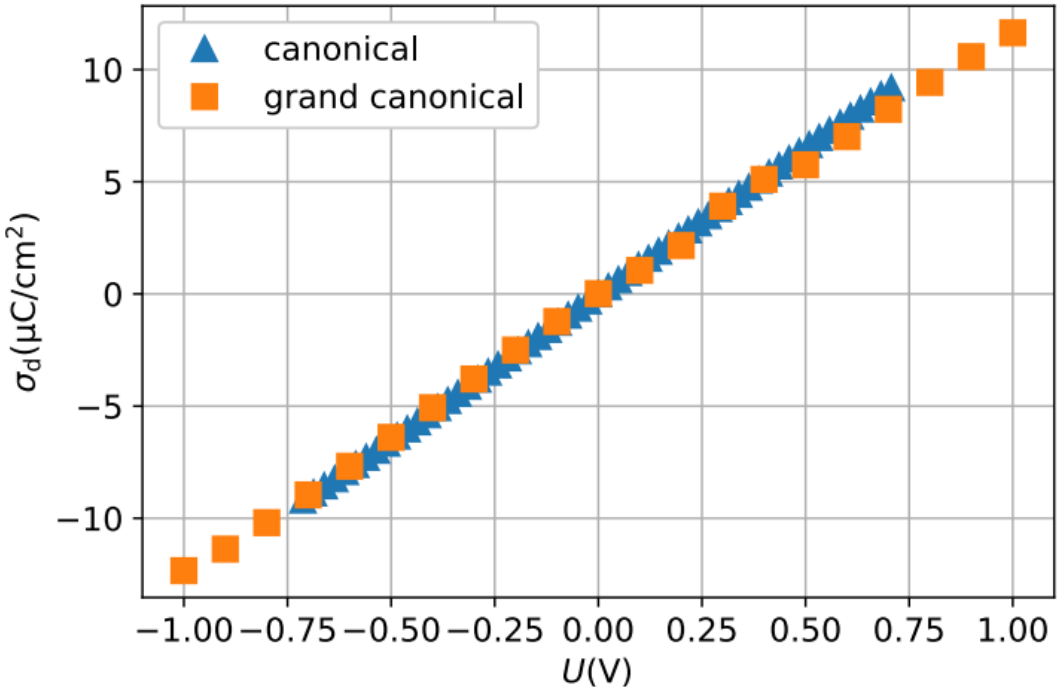
Submitted: 11 May 2021 • Accepted: 22 June 2021 • Published Online: 12 July 2021

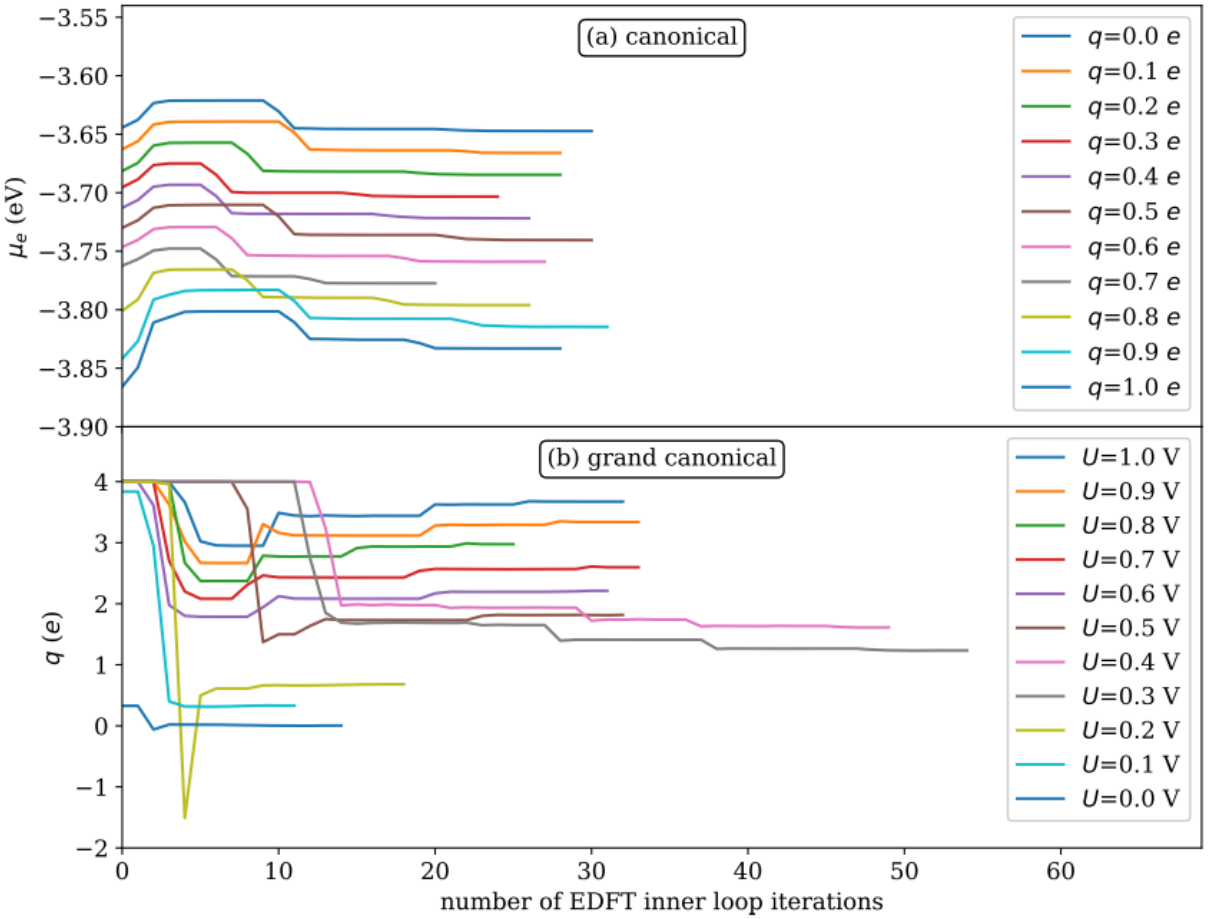
Arihant Bhandari, Chao Peng, Jacek Dziedzic, et al.

Model for simulations of electrified solid-liquid interfaces in ONETEP

- Ensemble for electrons

Canonical	Grand canonical
Electronically isolated system.	System connected with an electronic reservoir.
Number of electrons and the charge is fixed.	Chemical potential of electrons is fixed.
Chemical potential is found.	Charge is found.



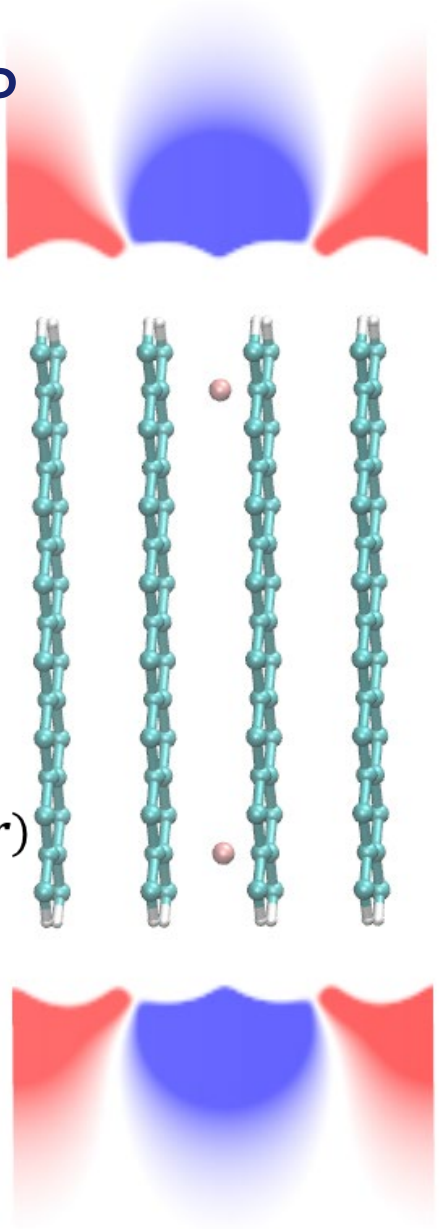


Model for simulations of electrified solid-liquid interfaces in ONETEP

- Electroneutrality $\nabla \cdot [\varepsilon(\boldsymbol{r})\nabla v(\boldsymbol{r})] = -4\pi[\rho(\boldsymbol{r}) + \rho_{mob}(\boldsymbol{r})]$

Jellium	Accessible Jellium	Grand canonical electrolyte
Opposite background charge in the entire simulation cell.	Opposite background charge in the electrolyte accessible region.	Non-uniform background charge which follows Poisson-Boltzmann distribution and neutralizes the charge on atoms.
$\rho_{\mathrm{mob}}(\boldsymbol{r}) = -\frac{\int \rho(\boldsymbol{r}')d\boldsymbol{r}'}{\int d\boldsymbol{r}'}$	$\rho_{\mathrm{mob}}(\boldsymbol{r}) = -\frac{\lambda(\boldsymbol{r})\int \rho(\boldsymbol{r}')d\boldsymbol{r}'}{\int \lambda(\boldsymbol{r}')d\boldsymbol{r}'}$	$\rho_{\mathrm{mob}}(\boldsymbol{r}) = \lambda(\boldsymbol{r})\sum_i z_i c_i^{\infty} \exp\left(\frac{-z_i[v(\boldsymbol{r}) + v_s]}{k_B T}\right)$

$$\lambda(\boldsymbol{r}) = \prod_I^N \frac{1}{2}\left[1 + \mathrm{erf}\left(\frac{|\boldsymbol{r} - \boldsymbol{R}_I| - R_I^{\lambda}}{\sigma}\right)\right]$$



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The Journal of Chemical Physics

Electronic structure calculations in electrolyte solutions: Methods for neutralization of extended charged interfaces

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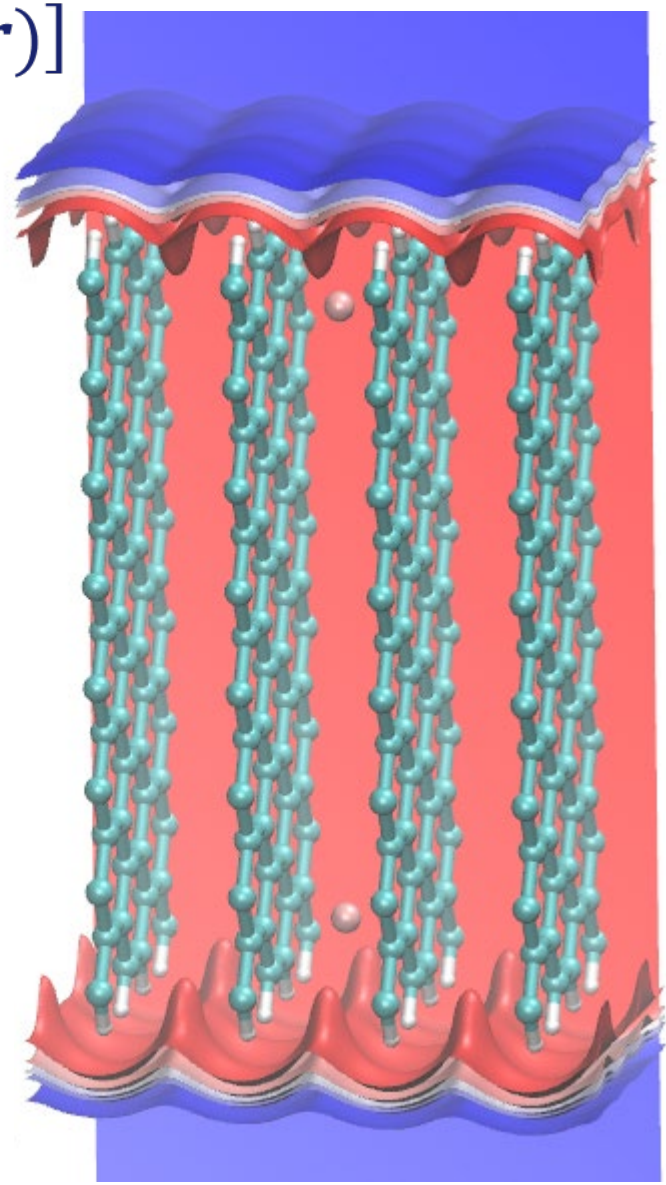
Arihant Bhandari, Lucian Anton, Jacek Dziedzic, Chao Peng, Denis Kramer, and Chris-Kriton Skylaris

Model for simulations of electrified solid-liquid interfaces in ONETEP

- Solvent medium $\nabla \cdot [\varepsilon(\boldsymbol{r})\nabla v(\boldsymbol{r})] = -4\pi[\rho(\boldsymbol{r}) + \rho_{mob}(\boldsymbol{r})]$

Vacuum	Solvent
Uniform permittivity of 1.0.	Permittivity varies smoothly from 1.0 near the atoms to that of the bulk solvent far away.
No interactions with the atoms.	Cavitation, dispersion and repulsion interaction proportional to the solvent accessible surface area.



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System

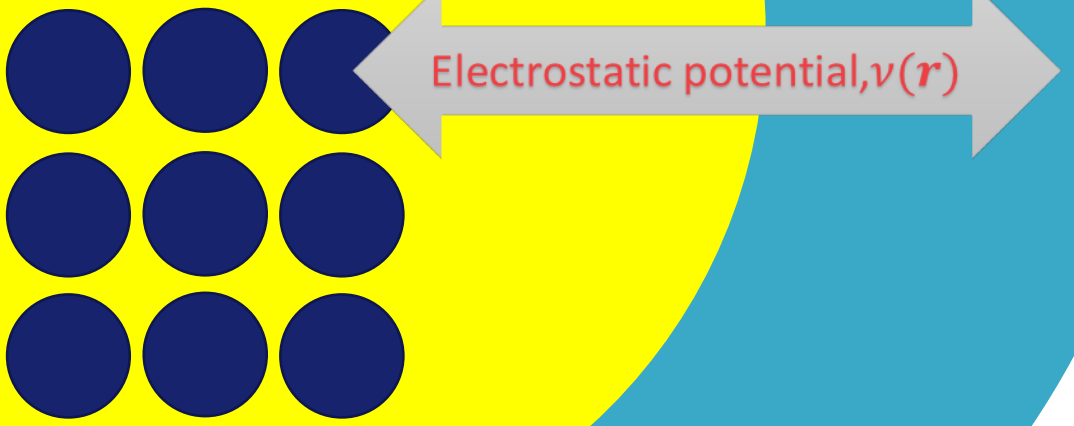
Quantum System

$\rho(\boldsymbol{r}) = \rho_{\mathrm{e}}(\boldsymbol{r}) + \rho_{\mathrm{nuc}}(\boldsymbol{r})$

$\rho_e(\boldsymbol{r}) = \sum_k f_k \psi_k(\boldsymbol{r})\psi_k^*(\boldsymbol{r})$

Dielectric solvent
and
Continuum electrolyte

$z_i, c_i(\boldsymbol{r}), i = 1 \ldots p$

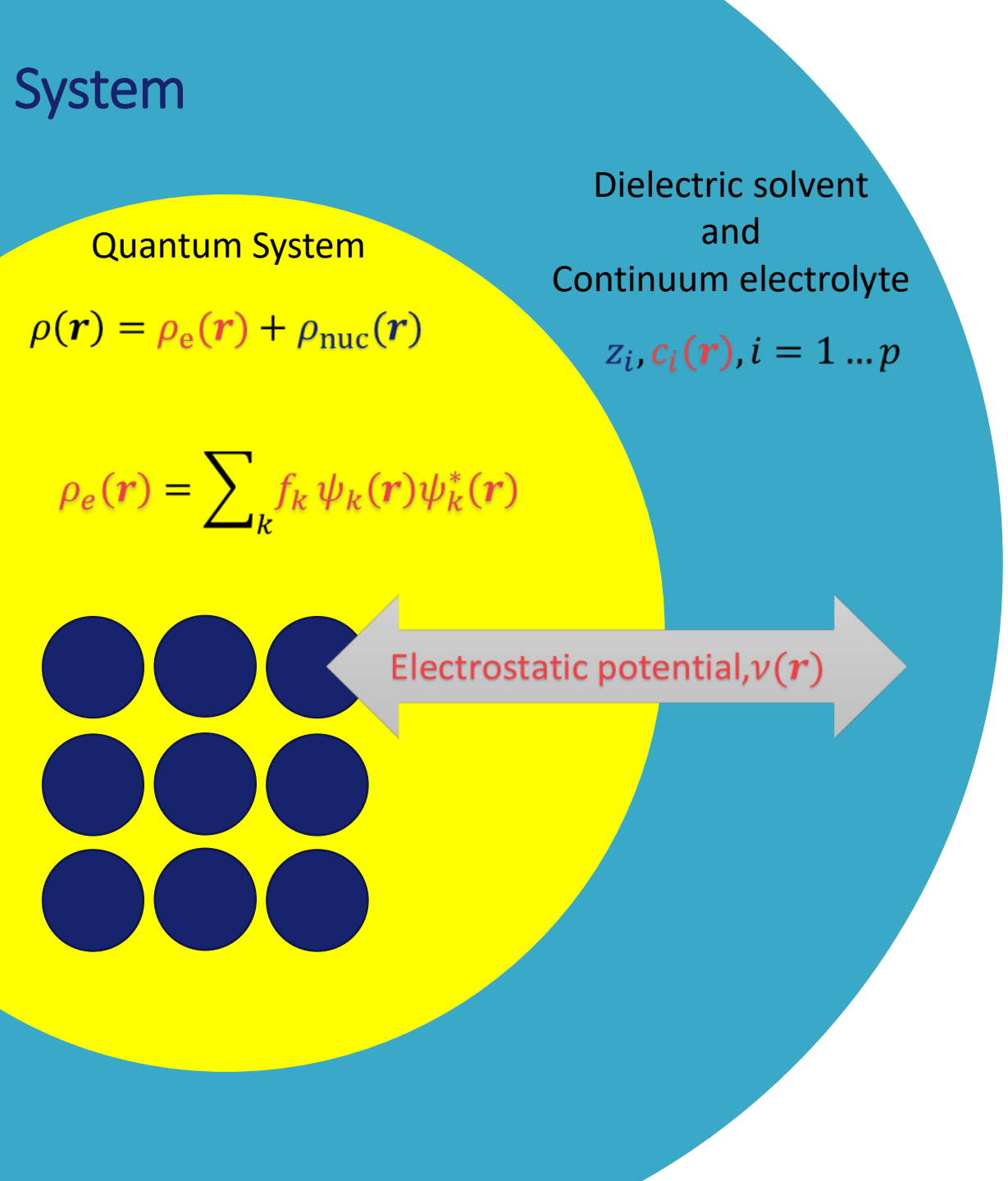


Electrostatic potential, $v(\boldsymbol{r})$

$$\Omega = \Omega_{\mathrm{e}}$$

$$+ \Omega_{\mathrm{mf}}$$

$$+ \Omega_{\mathrm{nmf}}$$



$$\Omega = \sum_k f_k \int \psi_k^*(\boldsymbol{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_k(\boldsymbol{r}) d\boldsymbol{r}$$ Kinetic energy

$$+k_B T \sum_k f_k \ln f_k + (1 - f_k) \ln f_k$$ Entropy

$$-\mu_{\mathrm{e}} \sum_k f_k$$ Chemical potential term

$$+ \sum_k f_k \int \psi_k^*(\boldsymbol{r})\, v_{\mathrm{ps}}(\boldsymbol{r})\, \psi_k(\boldsymbol{r}) d\boldsymbol{r}$$ Pseudopotential contribution

$$+E_{\mathrm{xc}}$$ Exchange Correlation Energy

System

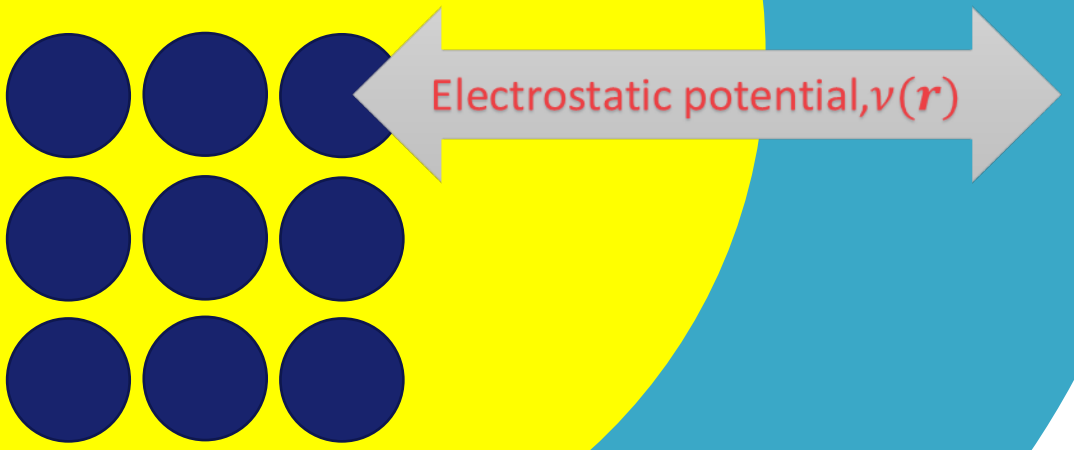
Quantum System

$\rho(\boldsymbol{r}) = \rho_{\mathrm{e}}(\boldsymbol{r}) + \rho_{\mathrm{nuc}}(\boldsymbol{r})$

$\rho_e(\boldsymbol{r}) = \sum_k f_k \, \psi_k(\boldsymbol{r}) \psi_k^*(\boldsymbol{r})$

Dielectric solvent
and
Continuum electrolyte

$z_i, c_i(\boldsymbol{r}), i = 1 \ldots p$



$$\Omega = \sum_k f_k \int \psi_k^*(\boldsymbol{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_k(\boldsymbol{r}) d\boldsymbol{r} \quad \text{Kinetic energy}$$

$$+k_B T \sum_k f_k \ln f_k + (1 - f_k) \ln f_k \quad \text{Entropy}$$

$$-\mu_{\mathrm{e}} \sum_k f_k \quad \text{Chemical potential term}$$

$$+\sum_k f_k \int \psi_k^*(\boldsymbol{r}) \, v_{\mathrm{ps}}(\boldsymbol{r}) \, \psi_k(\boldsymbol{r}) d\boldsymbol{r} \quad \text{Pseudopotential contribution}$$

$$+E_{\mathrm{xc}} \quad \text{Exchange Correlation Energy}$$

$$+\frac{1}{2} \int \left[\rho(\boldsymbol{r}) + \sum_i z_i \, c_i(\boldsymbol{r})\right] v(\boldsymbol{r}) d\boldsymbol{r} \quad \text{Electrostatic energy}$$

$$-k_B T \sum_{i=1}^{p} \int c_i(\boldsymbol{r}) d\boldsymbol{r} \quad \text{Electrolyte osmotic pressure}$$

$$-k_B T \sum_{i=1}^{p} \int c_i(\boldsymbol{r}) \ln \lambda(\boldsymbol{r}) \, d\boldsymbol{r} \quad \text{Electrolyte accessibility term}$$

$$+k_B T \sum_{i=1}^{p} \int c_i(\boldsymbol{r}) \ln \left(\frac{c_i(\boldsymbol{r})}{c^{\mathrm{o}}}\right) d\boldsymbol{r} \quad \text{Electrolyte entropy}$$

$$-\sum_{i=1}^{p} \mu_i \int c_i(\boldsymbol{r}) d\boldsymbol{r} \quad \text{Electrolyte chemical potential}$$

System

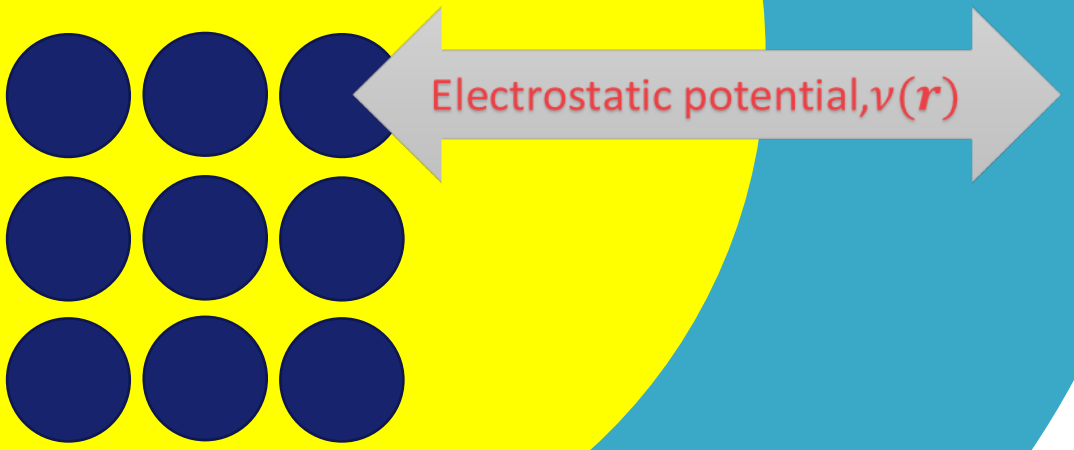
Quantum System

$\rho(\boldsymbol{r}) = \rho_{\mathrm{e}}(\boldsymbol{r}) + \rho_{\mathrm{nuc}}(\boldsymbol{r})$

$\rho_e(\boldsymbol{r}) = \sum_k f_k \, \psi_k(\boldsymbol{r}) \psi_k^*(\boldsymbol{r})$

Dielectric solvent
and
Continuum electrolyte

$z_i, c_i(\boldsymbol{r}), i = 1 \ldots p$



$$\Omega = \sum_k f_k \int \psi_k^*(\boldsymbol{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_k(\boldsymbol{r}) d\boldsymbol{r} \quad \text{Kinetic energy}$$

$$+k_B T \sum_k f_k \ln f_k + (1 - f_k) \ln f_k \quad \text{Entropy}$$

$$-\mu_{\mathrm{e}} \sum_k f_k \quad \text{Chemical potential term}$$

$$+ \sum_k f_k \int \psi_k^*(\boldsymbol{r}) \, v_{\mathrm{ps}}(\boldsymbol{r}) \, \psi_k(\boldsymbol{r}) d\boldsymbol{r} \quad \text{Pseudopotential contribution}$$

$$+E_{\mathrm{xc}} \quad \text{Exchange Correlation Energy}$$

$$+\frac{1}{2} \int \left[\rho(\boldsymbol{r}) + \sum_i z_i \, c_i(\boldsymbol{r})\right] v(\boldsymbol{r}) d\boldsymbol{r} \quad \text{Electrostatic energy}$$

$$-k_B T \sum_{i=1}^{p} \int c_i(\boldsymbol{r}) d\boldsymbol{r} \quad \text{Electrolyte osmotic pressure}$$

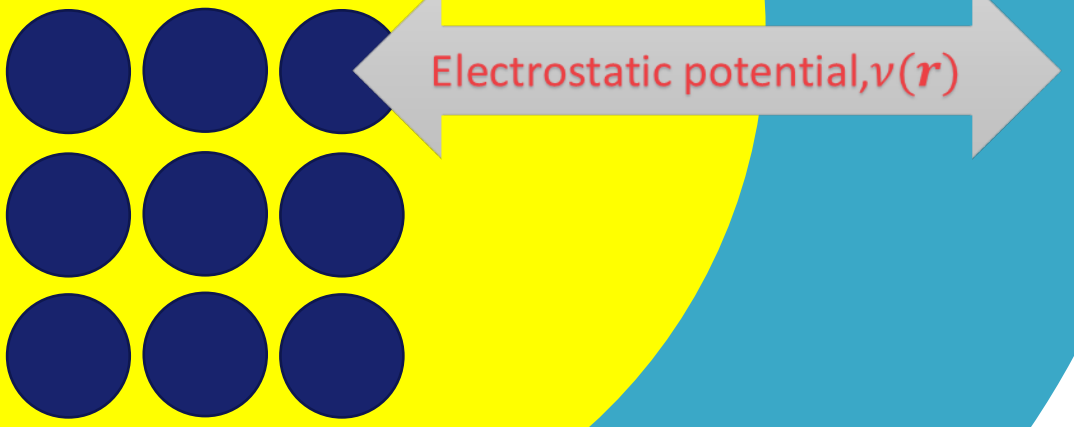
$$-k_B T \sum_{i=1}^{p} \int c_i(\boldsymbol{r}) \ln \lambda(\boldsymbol{r}) \, d\boldsymbol{r} \quad \text{Electrolyte accessibility term}$$

$$+k_B T \sum_{i=1}^{p} \int c_i(\boldsymbol{r}) \ln \left(\frac{c_i(\boldsymbol{r})}{c^{\mathrm{o}}}\right) d\boldsymbol{r} \quad \text{Electrolyte entropy}$$

$$-\sum_{i=1}^{p} \mu_i \int c_i(\boldsymbol{r}) d\boldsymbol{r} \quad \text{Electrolyte chemical potential}$$

$$+\gamma S \quad \text{Solvent cavitation, dispersion and repulsion}$$

System



Total free energy,

$$\Omega[\rho_{\mathrm{e}}(\boldsymbol{r}), c_i(\boldsymbol{r}), v(\boldsymbol{r})]$$

is minimized

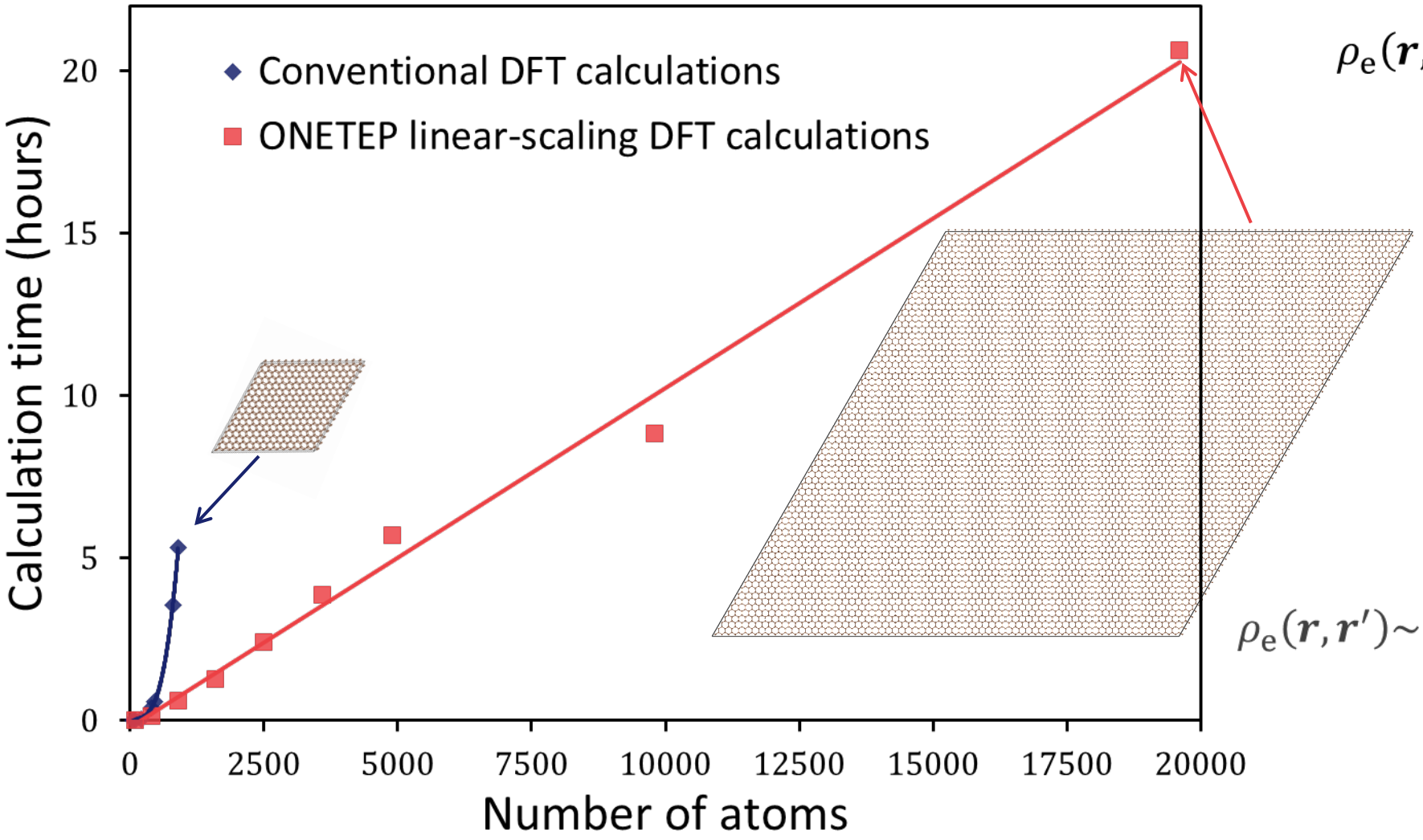
$$\left[-\frac{1}{2}\nabla^2 + v_{\mathrm{ps}}(\boldsymbol{r}) + v_{\mathrm{xc}}(\boldsymbol{r}) + v(\boldsymbol{r})\right]\psi_k = \varepsilon_k \psi_k$$

$$f_k = \frac{1}{1 + \exp\left(\frac{\varepsilon_k - \mu_{\mathrm{e}}}{k_{\mathrm{B}}T}\right)}$$

$$\nabla.[\varepsilon(\boldsymbol{r})\nabla v(\boldsymbol{r})] = -4\pi\left[\rho_{\mathrm{e}}(\boldsymbol{r}) + \rho_{\mathrm{nuc}}(\boldsymbol{r}) + \sum_{i=1}^{p} z_i c_i(\boldsymbol{r})\right]$$

$$c_i(\boldsymbol{r}) = c^0 \lambda(\boldsymbol{r}) \exp\left(-\frac{z_i v(\boldsymbol{r})}{k_B T} + \frac{\mu_i}{k_B T}\right)$$

ONETEP: quantum atomistic (Density Functional Theory - DFT) program with unique linear-scaling computational effort with the number of atoms



$$\rho_e(\boldsymbol{r},\boldsymbol{r}') = \sum_k f_k\, \psi_k(\boldsymbol{r})\psi_k^*(\boldsymbol{r}')$$

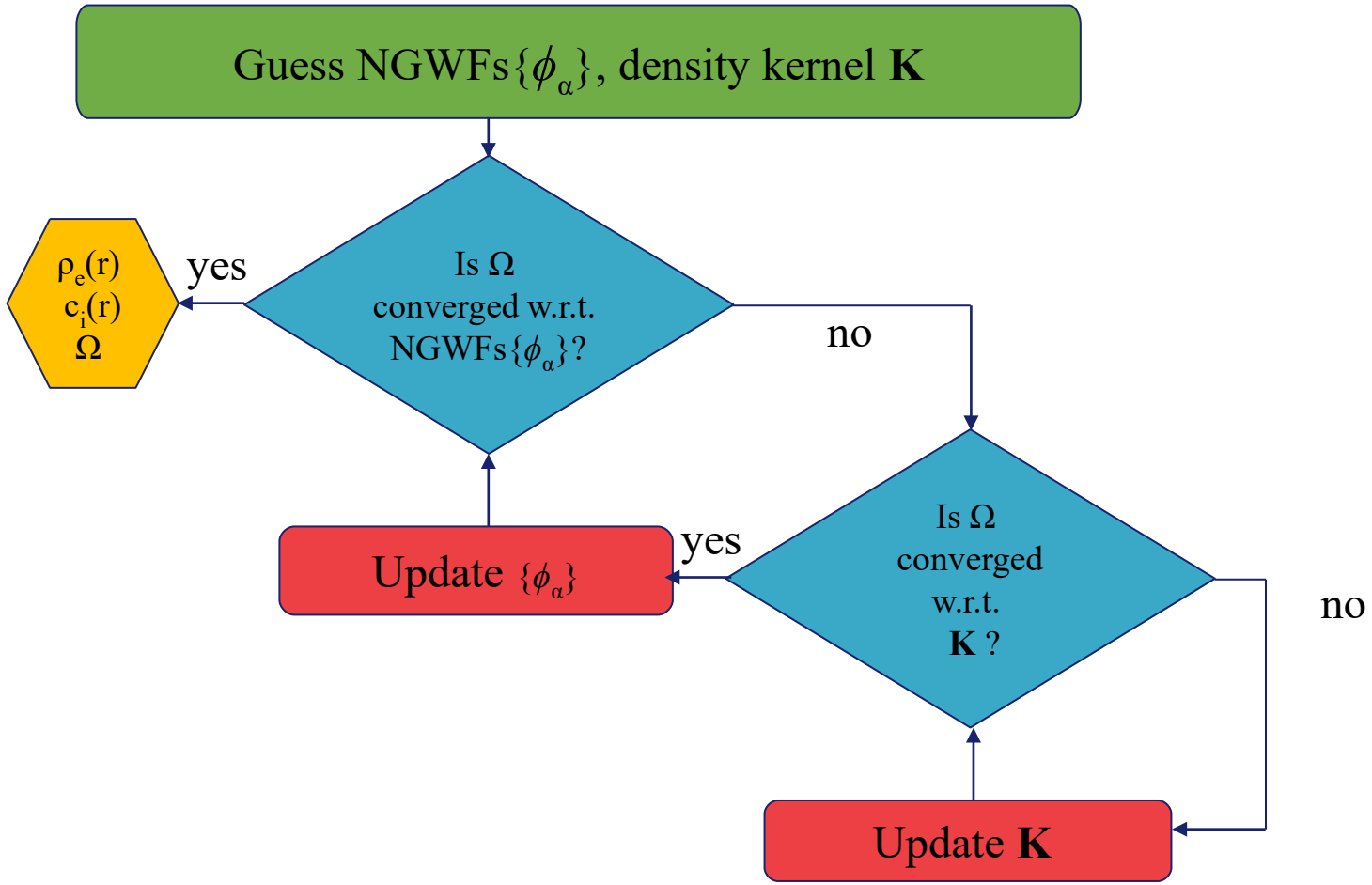
Molecular orbitals

$$= \sum_{\alpha,\beta} \phi_\alpha(\boldsymbol{r}) K^{\alpha\beta} \phi_\beta(\boldsymbol{r}')$$

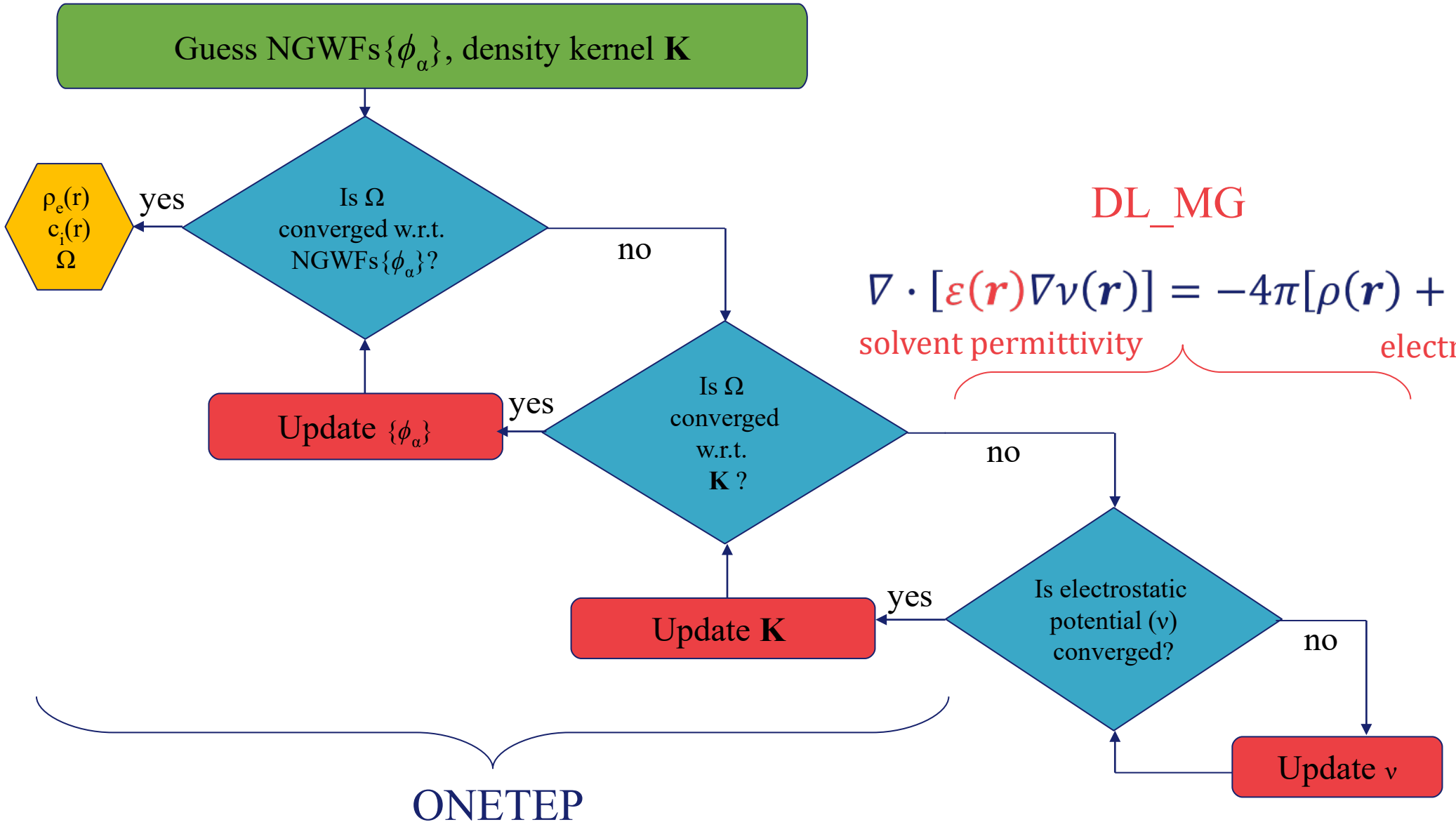
NGWFs

$$\rho_e(\boldsymbol{r},\boldsymbol{r}') \sim e^{-\gamma|r-r'|} \to 0, \text{as } |\boldsymbol{r}-\boldsymbol{r}'| \to \infty$$

ONETEP Calculation procedure in vacuum



ONETEP Calculation procedure with new electrolyte model



DL_MG

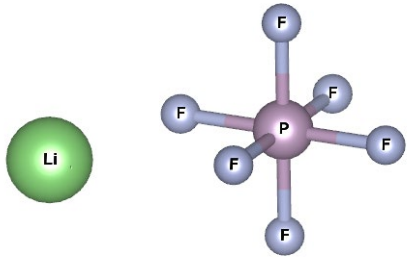
$$\nabla \cdot [\varepsilon(\boldsymbol{r})\nabla v(\boldsymbol{r})] = -4\pi[\rho(\boldsymbol{r}) + \rho_{mob}(\boldsymbol{r})]$$

solvent permittivity

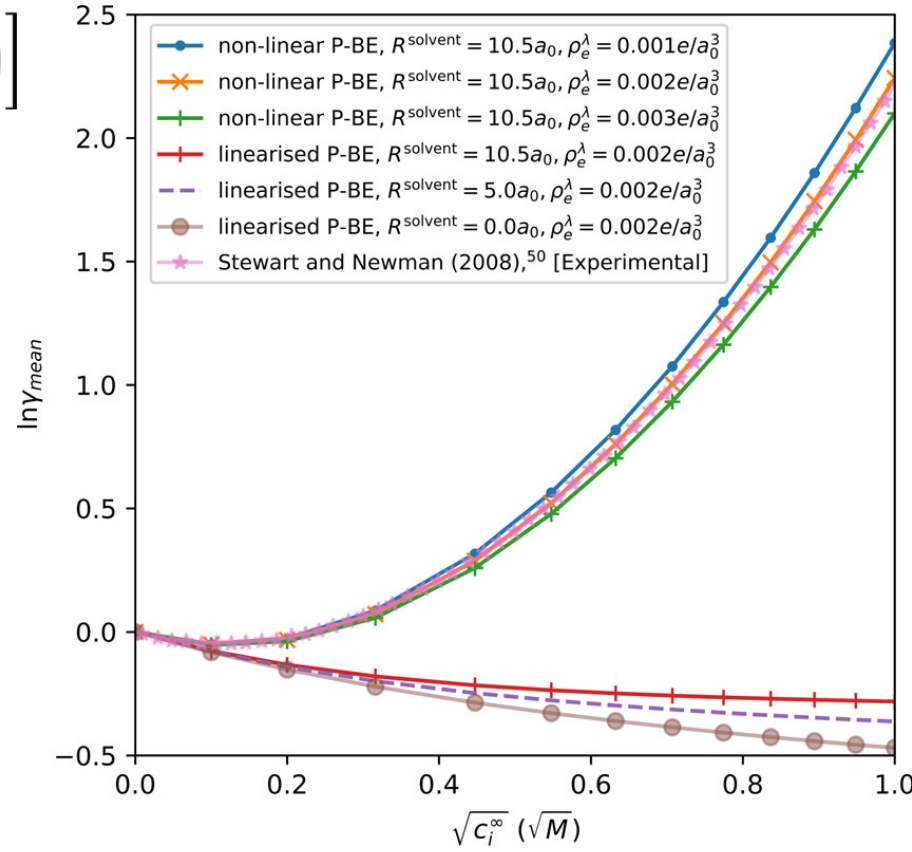
electrolyte charge

Electrolyte Parameters

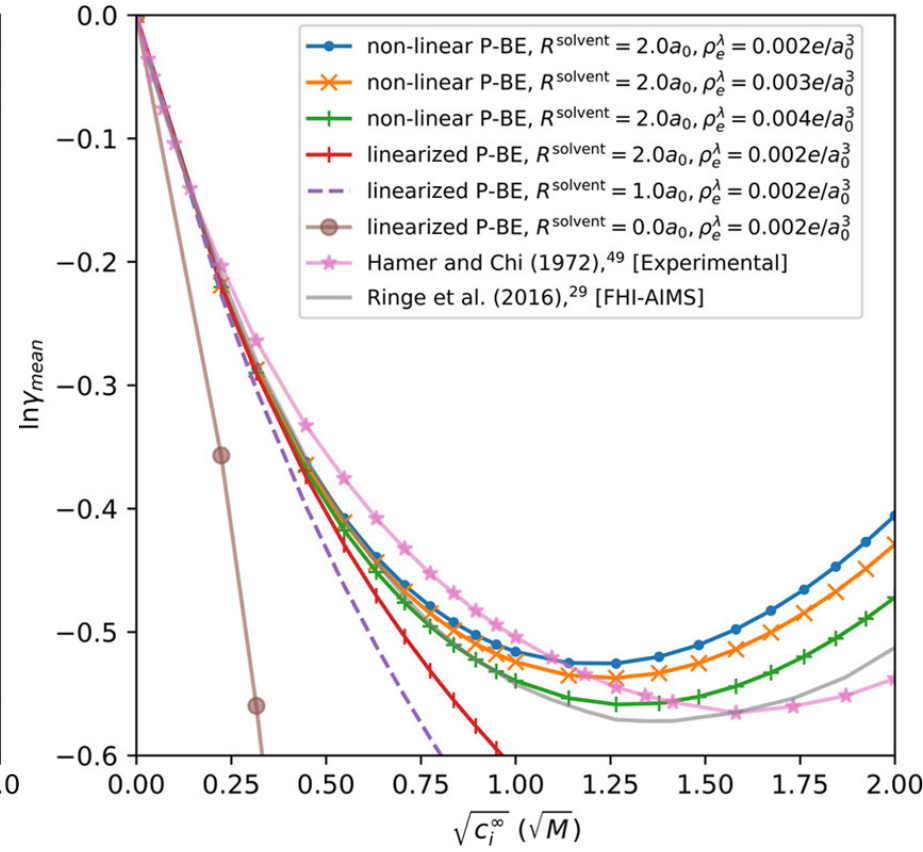
- $\lambda(\boldsymbol{r}) = \prod_I^N \frac{1}{2}\left[1 + \mathrm{erf}\left(\frac{|\boldsymbol{r}-\boldsymbol{R}_I| - R_I^\lambda}{\sigma}\right)\right]$
- $R_I^\lambda = R^{\mathrm{solute}}(\rho_e^\lambda) + R^{\mathrm{solvent}}$
- Mean activity coefficients from
- Solvation free energies ($\Delta\Omega_i$)



- $\ln \gamma_i = \frac{\Delta\Omega_i(c_i^\infty) - \Delta\Omega_i(c_i^\infty = 0)}{k_B \mathrm{T}}$
- $\ln \gamma_{\mathrm{mean}} = \frac{1}{p}\sum_{1=1}^{p} \ln \gamma_i$



$LiPF_6$ in EC at 308 K



KCl in water at 298 K

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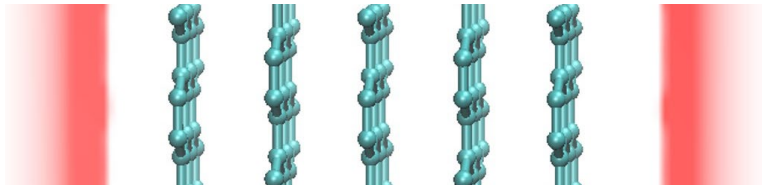
Practical Approach to Large-Scale Electronic Structure Calculations in Electrolyte Solutions via Continuum-Embedded Linear-Scaling Density Functional Theory

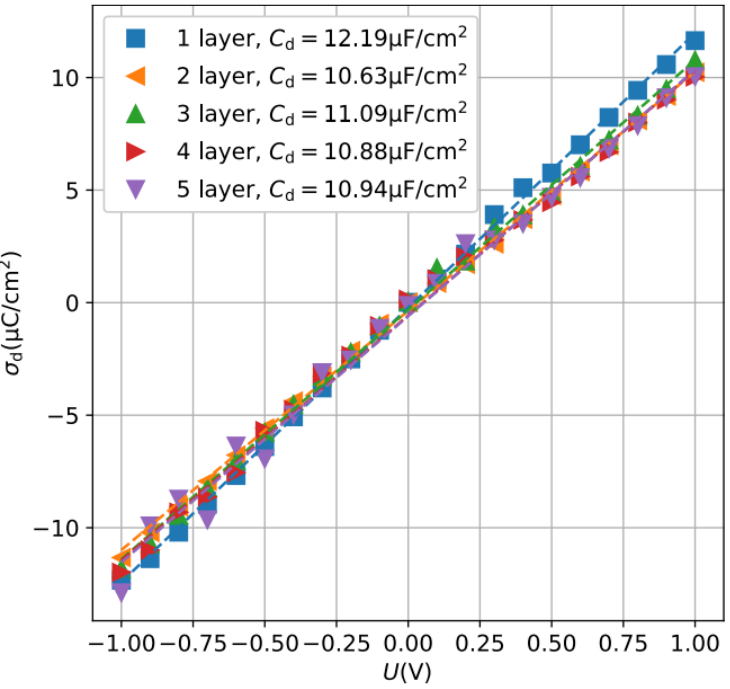
Jacek Dziedzic, Arihant Bhandari, Lucian Anton, Chao Peng, James C. Womack, Marjan Famili, Denis Kramer, and Chris-Kriton Skylaris*

Cite This: *J. Phys. Chem. C* 2020, 124, 7860−7872 Read Online

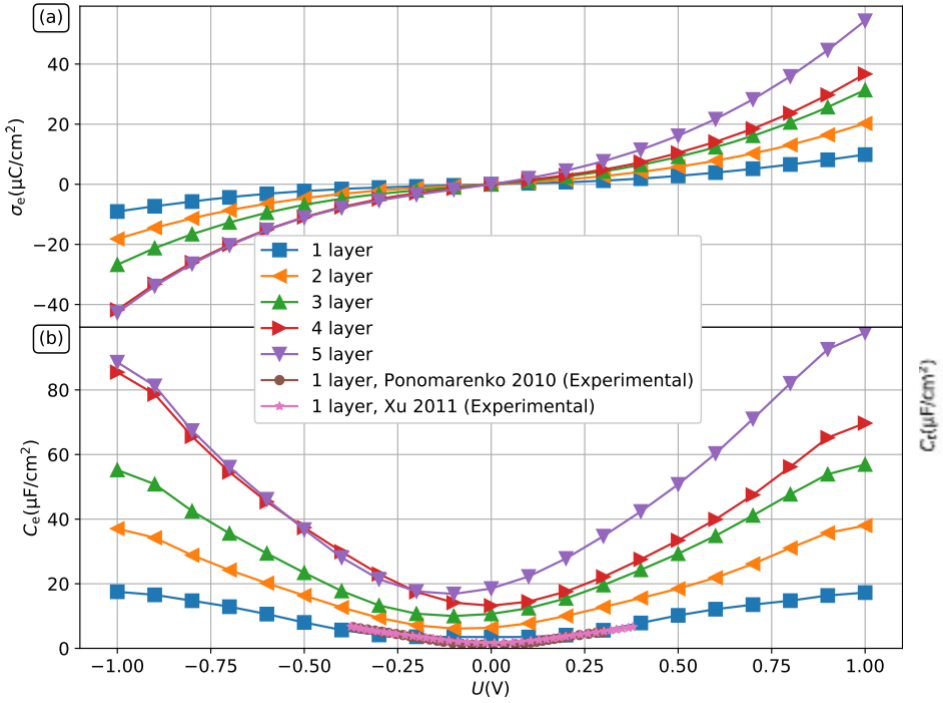
Differential capacitance of few-layer graphene



Diffuse layer capacitance



Electronic capacitance



The Journal of Chemical Physics ARTICLE scitation.org/journal/jcp

Electrochemistry from first-principles in the grand canonical ensemble

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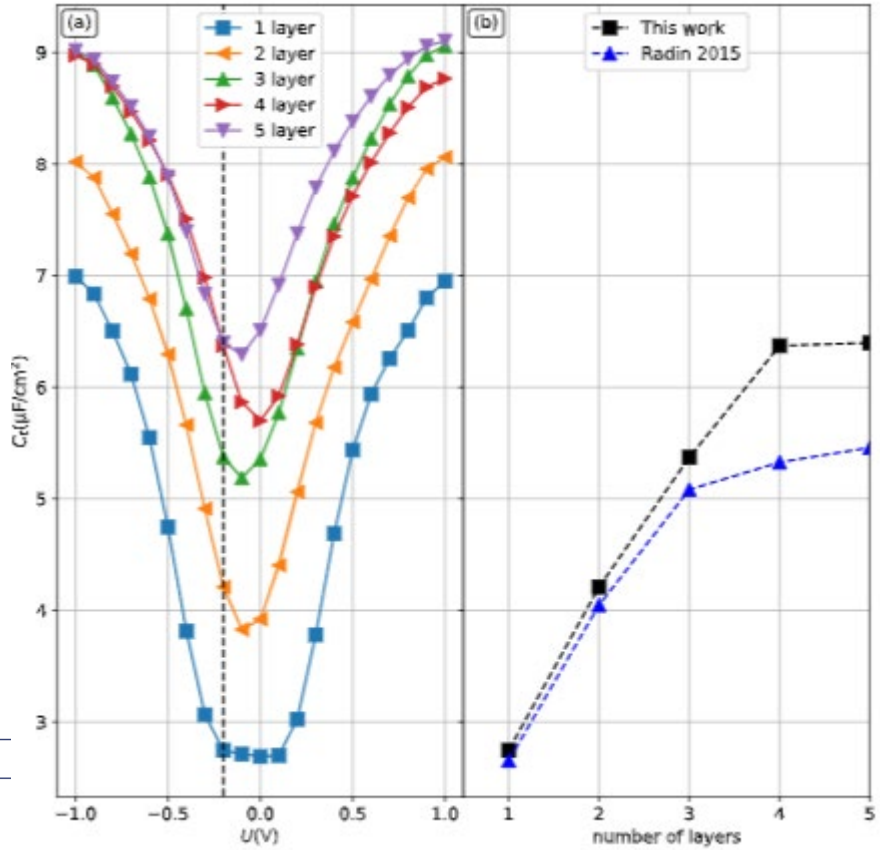
Published Online: 12 July 2021

Arihant Bhandari,[1,2] Chao Peng,[3,2] Jacek Dziedzic,[1,4,2] Lucian Anton,[5] John R. Owen,[1,2] Denis Kramer,[3,2,6] and Chris-Kriton Skylaris[1,2,a)]

Total capacitance $\frac{1}{C_t} = \frac{1}{C_d} + \frac{1}{C_e}$



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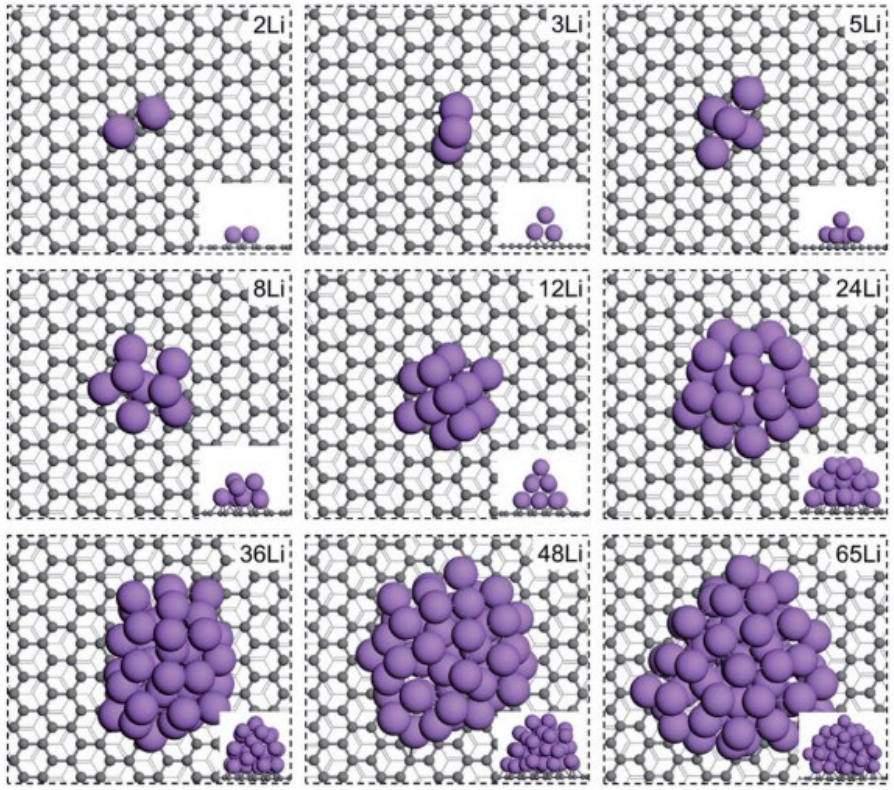
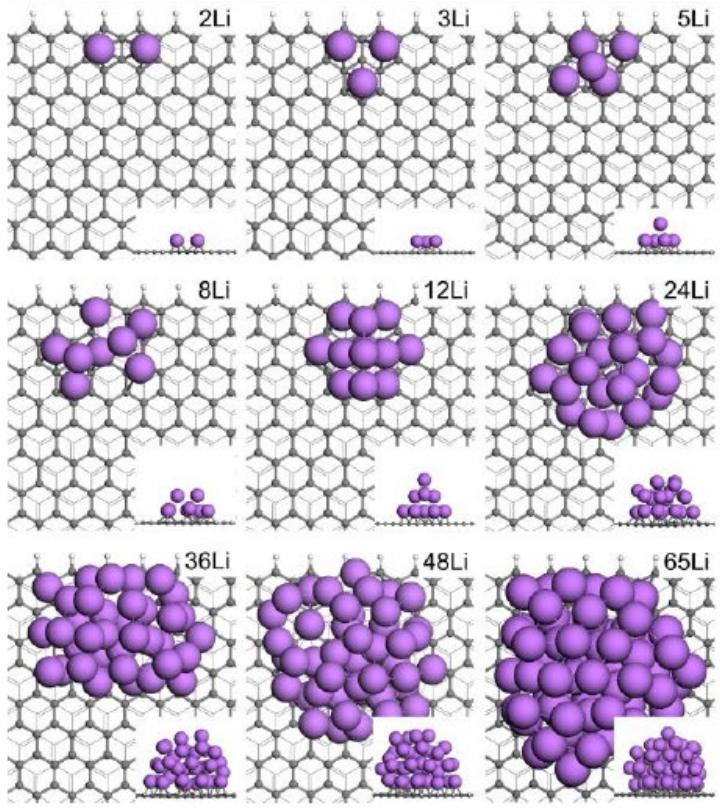
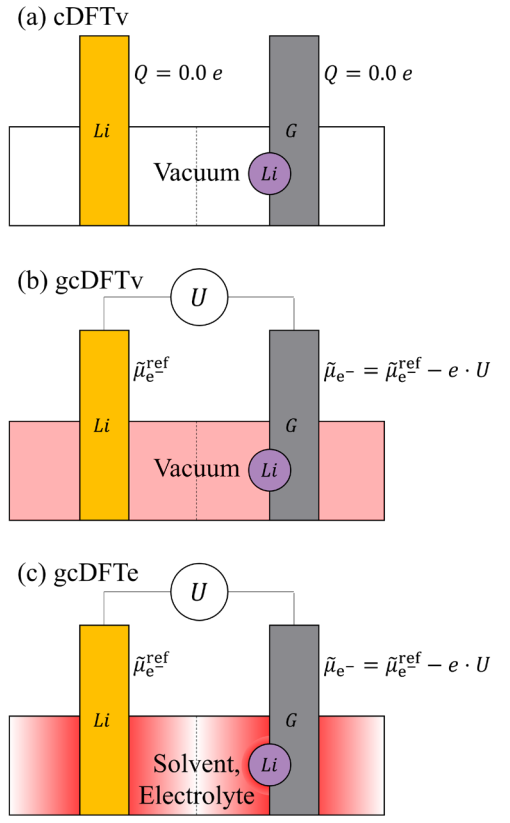
Critical voltage for degradation due to dendrite growth in Li-ion batteries

- On extended basal plane



- Close to zigzag edge





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Journal of Materials Chemistry A

ROYAL SOCIETY OF CHEMISTRY

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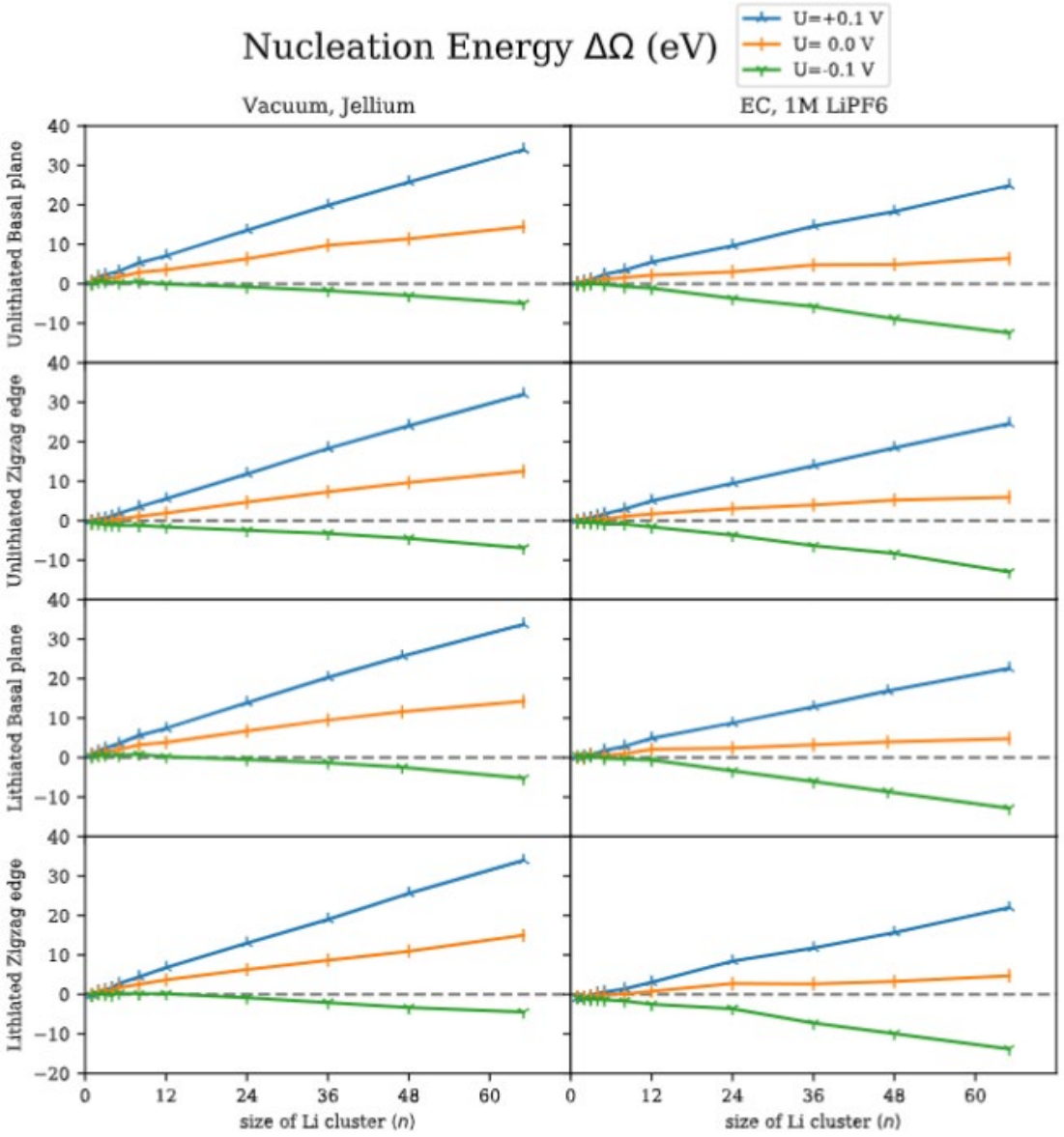
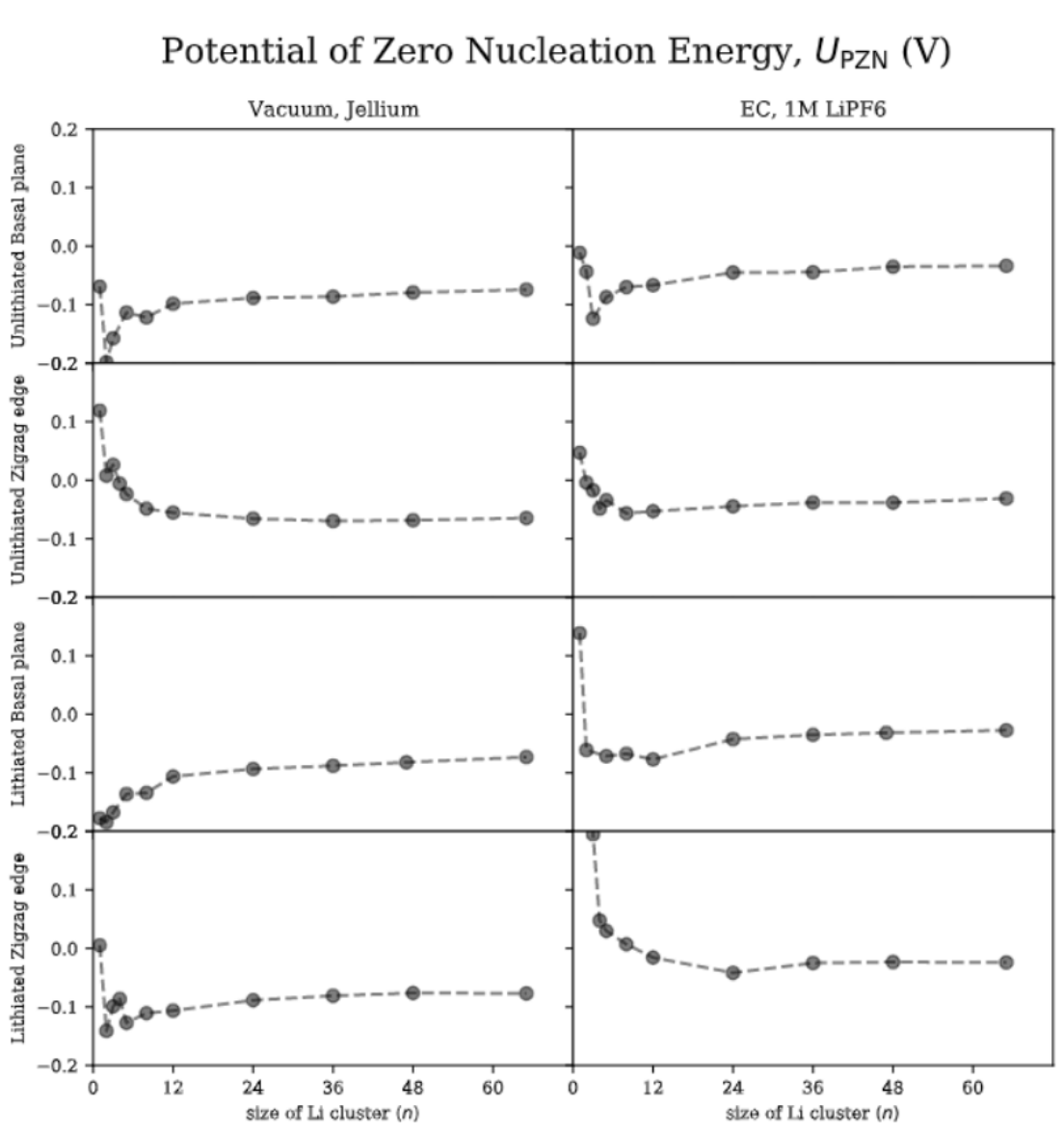
Li nucleation on the graphite anode under potential control in Li-ion batteries†

Arihant Bhandari, [ab] Chao Peng, [bc] Jacek Dziedzic, [abd] John R. Owen, [ab] Denis Kramer [bce] and Chris-Kriton Skylaris [*ab]

Nucleation Energy

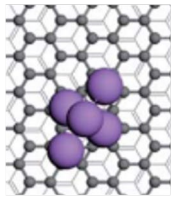
$$n\,Li + G \rightarrow Li_nG,$$
$$\Delta\Omega(U) = \left[\Omega_{Li_n|G}(U) - \Omega_G(U) - n \cdot \left(\tilde{\mu}_{Li}^{\mathrm{ref}}\right)\right]$$



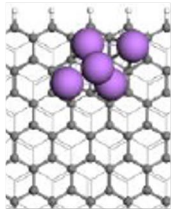


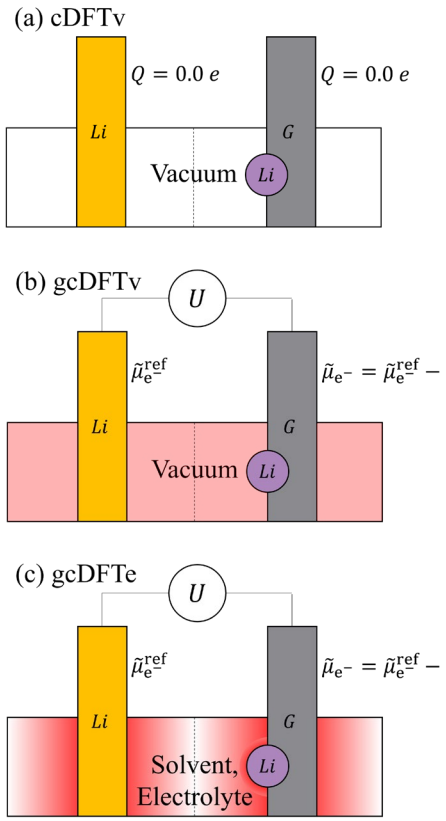
Critical voltage for degradation due to dendrite growth in Li-ion batteries

Basal plane of graphite



Zigzag edge of graphite





System	Ensemble	Canonical	Grand canonical		Experiment
	Environment	Vacuum (cDFTv)	Vacuum, Jellium (gcDFTv)	EC, 1M $LiPF_6$ (gcDFTe)	EC/DEC, 1M $LiPF_6$
Unlithiated graphite	Basal Plane	-0.65 V	-0.20 V	-0.12 V	-0.15 to -0.04 V Gao et al. Joule 5, 393–414, (2021)
	Zigzag edge	-0.31 V	-0.07 V	-0.06 V	
Lithiated graphite	Basal Plane	N.A.	-0.18 V	-0.08 V	
	Zigzag edge	-0.47 V	-0.14 V	-0.04 V	

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Journal of Materials Chemistry A

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Li nucleation on the graphite anode under potential control in Li-ion batteries†

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Scope for improvements

- Accessibility function independent of type of electrolyte ion (i)

$$c_i(\boldsymbol{r}) = \lambda(\boldsymbol{r}) c_i^{\infty} \exp\left[-\frac{z_i \nu(\boldsymbol{r})}{k_B T}\right]$$

- Point size of electrolyte ions. Finite size effects can be included with a sterically modified Poisson-Boltzmann equation, which limits the maximum concentration $(c_{\max})$ of electrolyte ions.

$$c_i(\boldsymbol{r}) = \frac{\lambda(\boldsymbol{r}) c_i^{\infty} \exp\left[-\frac{z_i \nu(\boldsymbol{r})}{k_B T}\right]}{1 - \sum_i \frac{c_i^{\infty}}{c_{\max}} \left(1 - \exp\left[-\frac{z_i \nu(\boldsymbol{r})}{k_B T}\right]\right)}$$

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Questions