Large-scale DFT in solution:  
*Just add implicit solvent*

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Outline

- Implicit solvent
- The need for solvent
- Theoretical design
- Validation

- Large-scale DFT
- The model
- Self-consistent reaction field

- Background
- Validation

- ONETEP
- DFT package
- Multigrid solver

- Implementation
- Boundary conditions

- Large-scale DFT in solution

Image of complex: Fig. 1 from D.J. Cole, A.W. Chin, N.D.M. Hine, P.D. Haynes, and M.C. Payne, J. Phys. Chem. Lett. 4, 4206 (2013) [CC-BY-4.0 license].
Large-scale density functional theory

Incredibly successful and widely used method!
- Relatively low computational cost
- Includes electron correlation in a SCF model
- Facilitated by
  - Modern parallel computer hardware
  - Efficient theoretical methods / approximations

\[ E_{KS}[n] = T_s[n] + E_{ext}[n] + E_{Hartree}[n] + E_{xc}[n] \]

\[ n(r) = \sum_i \psi_i(r)\psi^*_i(r) \]

\[ \left(-\frac{1}{2}\nabla^2 + V_{KS}(r)\right)\psi_i(r) = \varepsilon_i\psi_i(r) \]

\[ V_{KS}(r) = V_{ext}(r) + V_{Hartree}(r) + V_{xc}(r) \]

DFT studies of extended systems are now possible using routinely available computational resources...

Images: Polymer from G. Boschietto, Pt_{309}O_{63} from L. Verga.
Large-scale density functional theory

Linear-scaling density matrix DFT

$$\rho(r, r') = \sum_i^N f_i \psi_i(r) \psi_i^*(r')$$

$$\rho(r, r) = n(r)$$

- The density matrix is “nearsighted”
- For insulators: $\rho(r, r') \sim e^{-\gamma|r-r'|}$

Exploit this to obtain linear scaling computational cost

Order-N Electronic Total Energy Package

$$\rho(r, r') = \sum_{\alpha\beta} \varphi_\alpha(r) K^{\alpha\beta} \varphi_\beta^*(r')$$

Non-orthogonal generalized Wannier functions (NGWFs)

- Strictly localized
- Self-consistently optimized

Large basis set accuracy possible with a minimal set of NGWFs!

Density kernel truncated above cut-off length

$$R^{\alpha\beta} > r_{cut} \rightarrow K^{\alpha\beta} = 0$$

3 Structure from authors of J.T. Berryman et al., Biophys. J. 97, 1 (2009)
The need for solvation

- Theorists like to think matter exists in a vacuum
  - No environment to consider
  - Theoretical simplifications possible
- But many natural and artificial systems exist in solution
  - The environment can significantly affect the behaviour of molecules and their reactions
- Simulations which account for solvent effects allow us to address new questions, e.g.
  - How is the activity of my catalyst impacted by the solvent used?
  - How does the cell environment affect the folding of this protein?
  - How will this pharmaceutical behave when dissolved in the stomach?

Image: "Acid & base test using vinegar", courtesy of Carolina Biological Supply Company (www.flickr.com/carolinabio)
**Approaches to solvation in DFT**

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Solute interacts with individual solvent molecules

+ Detailed description of solute-solvent interactions
+ Can describe solvent structural effects, e.g. H-bonding
- Increase in system size, $N$, and computational cost
- Need to statistically average solvent degrees of freedom
- Solvent-solvent interactions must be treated

Solute interacts with implicit representation of solvent

+ Do not increase system size, $N$, compared to solute.
+ Solvent degrees of freedom implicitly averaged
+ Avoid explicit treatment of solvent-solvent interactions
- Solvent structural effects are generally not described
- Specific solute-solvent interactions not accounted for
- Typically require empirical parameterization

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Explicit and implicit approaches can also be combined...

**Continuum dielectric implicit solvent**

Many possible approaches, see e.g. 1 & 2

Focus of this work

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Reviews on implicit solvation:
Continuum dielectric model

$$E_{es}[n] = \frac{1}{2} \int \mathbf{dr} n(\mathbf{r}) \phi_{es}[n](\mathbf{r})$$

Potential due to solute charge

$$\int \mathbf{dr}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$\nabla^2 \phi_0(\mathbf{r}) = -4\pi n(\mathbf{r})$$

Standard Poisson equation (SPE)

$$\phi_{es}(\mathbf{r}) = \phi_0(\mathbf{r}) + \phi_r(\mathbf{r})$$

“Solvent reaction potential”

$$\int \mathbf{dr}' \frac{\mathbf{P}(\mathbf{r}') \cdot (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3}$$

Potential due to dielectric medium

$$\nabla \cdot (\varepsilon[n](\mathbf{r}) \nabla \phi_{es}(\mathbf{r})) = -4\pi n(\mathbf{r})$$

Generalized Poisson equation (GPE)

As described in:
Continuum dielectric **Self-Consistent Reaction Field**

\[
E_{\text{KS-SCRF}}[n] = T_s[n] + E_{\text{ext}}[n] + E_{xc}[n] + E_{es}[n] + \Delta G_{\text{non-es}}[n]
\]

Initial guess \( n(r) \)

Solve KS equations

Determine reaction potential

Converged result \( n_{\text{elec}}(r) + n_{\text{ion}}(r) \)

Obtain reaction potential by solving GPE:

\[
\nabla \cdot (\varepsilon[n](r) \nabla \phi_{es}(r)) = -4\pi n(r)
\]

A general method for self-consistent solution for the solute charge and reaction potential

Well-established methods have been developed, e.g. PCM\(^1\), COSMO\(^2\) and variants\(^3\).

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Minimal Parameter Implicit Solvent Model

Solute charge
- From density functional theory
- Smeared ionic core charges

\[ n_{\text{elec}}(\mathbf{r}) = \sum_i \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}) \]
\[ n(\mathbf{r}) = n_{\text{elec}}(\mathbf{r}) + n_{\text{ion}}(\mathbf{r}) \]

Cavity
- Density dependent
- Smoothly varying dielectric function
- Two fitted parameters: \( \beta, n_0 \)

\[ \varepsilon(\mathbf{r}) = 1 + \frac{\varepsilon_\infty - 1}{2} \left( 1 + \frac{1 - (n_{\text{elec}}(\mathbf{r})/n_0)^{2\beta}}{1 + (n_{\text{elec}}(\mathbf{r})/n_0)^{2\beta}} \right) \]

Non-electrostatic part
- From cavity surface area
- Effective surface tension accounts for dispersion-repulsion

\[ \Delta G_{\text{non-es}} = \gamma_{\text{eff}} S[n_{\text{elec}}] \]

\[ \nabla \cdot (\varepsilon(\mathbf{r}) \nabla \phi(\mathbf{r})) = -4\pi n(\mathbf{r}) \]

A refined “Fattebert-Gygi-Scherlis” (FGS) model
- Self-consistently solve KS equations subject to solvent
- Electrostatic/non-electrostatic terms depend on density

MPSM in ONETEP: Demonstrating the model

Testing the model in ONETEP for 71 neutral molecules*

<table>
<thead>
<tr>
<th>Approach</th>
<th>XC functional</th>
<th>RMS error</th>
<th>Max error</th>
<th>R</th>
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<tr>
<td>MPSM(^a)</td>
<td>PBE</td>
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<td>8.3</td>
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<td>MPSM(^b)</td>
<td>PBE</td>
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<td>M05-2X</td>
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<td>AMBER (classical)</td>
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<td>19.9</td>
<td>0.77</td>
</tr>
</tbody>
</table>

Free energies of solvation in \(H_2O\), kcal/mol

\(^a\)Self-consistent cavity, \(^b\)Fixed cavity

PCM\(^4\), SMD\(^5\) and AMBER\(^6\) force field Poisson-Boltzmann are competing implicit solvent models.

See Ref 7 for more calculation details.

* Taken from blind tests in
Experimental energies of solvation from
3 Minnesota solvation database, version 2009

4 S. Miertuš et al., Chem. Phys. 55, 117 (1981)
7 J. Dziedzic et al., EPL 95, 43001 (2011)
An accurate, scalable multigrid Poisson solver library\textsuperscript{1,3}

- Efficient real-space solution to second-order using multigrid
- Highly parallelised: MPI + OpenMP
- Input and output on real-space Cartesian grid
- Multiple equations: SPE, GPE, Poisson-Boltzmann
- Periodic, open and mixed boundary conditions
- Higher-order accuracy via defect correction approach\textsuperscript{2,3}

### Multigrid solver\textsuperscript{3}

*Improve convergence of conventional numerical solvers by employing a hierarchy of coarsening grids.*

- Solve for arbitrary $n(\mathbf{r})$ on 3-D grid
- Rapid convergence of error
- Excellent scaling wrt $N_{\text{grid}}$

### Accurate: Solving the SPE for a graphene sheet

\[ \nabla^2 \phi(\mathbf{r}) = -4\pi n(\mathbf{r}) \]

- ONETEP with DL_MG
- 448 atom periodic sheet
- PBE XC functional
- Norm-conserving PSPs
- $256 \times 264 \times 240$ grid
- Error wrt analytic solution

### Scalable: Solving the GPE in synthetic tests

\[ \nabla \cdot (\varepsilon(\mathbf{r}) \nabla \phi(\mathbf{r})) = -4\pi n(\mathbf{r}) \]

- Simple test case for benchmarking\textsuperscript{2}
  - Known analytic solution
- Efficient scaling
  - Up to $\sim 10^9$ grid points

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\textsuperscript{1} L. Anton, J. Dziedzic, C.-K. Skylaris, and M. I. J. Probert, “Multigrid Solver Module for ONETEP, CASTEP and Other Codes” (dCSE, 2013)


\textsuperscript{3} U. Trottenberg, C. W. Oosterlee, and A. Schüller, Multigrid, Academic Press, 2001
Boundary conditions

Flexible BCs enable study of diverse systems

- Consistent BCs in vacuum/solvent required for accurate $\Delta G_{\text{sol}}^{1}$
- Requires more than solving Poisson equation in different BCs
- Type of BCs needed depends on the system being studied

<table>
<thead>
<tr>
<th>Periodicity</th>
<th>Examples</th>
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<tbody>
<tr>
<td>0-D (open)</td>
<td>Protein Nanoparticle</td>
</tr>
<tr>
<td>1-D</td>
<td>Nanowire Polymer</td>
</tr>
<tr>
<td>2-D</td>
<td>Heterogeneous catalyst</td>
</tr>
<tr>
<td></td>
<td>Electrode surface</td>
</tr>
<tr>
<td>3-D (full)</td>
<td>Crystal molecular sieve</td>
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</table>

Periodic BC solvation

Only fully open BC solvation available previously in ONETEP MPSM
- Full PBC solvation now available
- Step toward mixed open/periodic BCs

- Solvation in $H_2O$ (kcal/mol)
- PBE XC functional
- Norm-conserving PSPs
- 800 eV KE cutoff
- Fixed dielectric cavity

Free energy of solvation, $\Delta G_{\text{sol}}$

"the reversible work required to transfer the solute in a fixed configuration from vacuum to solution"

$E_{\text{elec}}[n_{\text{tot}}] = \frac{1}{2} \int \text{d}r n_{\text{tot}}(r) \phi[n_{\text{tot}}(r)] + (E_{\text{loc}} \rho_{\text{elec}} - E_{\text{si-elec}} n_{\text{elec}}) + (E_{\text{ion-ion}} - E_{\text{si-si}})$

BCs must be consistently treated in each term!


Image: Pt on graphene from L. Verga.
Fixing vanishing HOMO-LUMO gaps in water clusters

- Lever et al. used ONETEP to investigate vanishing gaps in proteins and water clusters.\(^1\)
- Convincingly demonstrated that this is an electrostatic effect.
  - Implicit solvent can remedy this issue.

Band gaps for spherical water clusters

- Extracted from 50 Å water cube
- Equilibrated using classical MD
- Expect gap to tend to bulk value as size increases

Electrostatic potential

- 16 Å water cluster
- Slice 24.6 Å behind cluster
- -0.3 V (red)
- +0.3 V (blue)

Implicit solvent restores the band gap by screening the electrostatic potential over the cluster

“While the molecular dipoles inside the cluster are oriented so as to mostly cancel any long-ranged effect, those on the surface are not compensated by their neighbours, so a large cluster will retain a large net dipole moment.”\(^1\)

Adapted from Figs. 1 & 2 [cropped] from “Electrostatic considerations affecting the calculated HOMO–LUMO gap in protein molecules”. \(^1\)

Large-scale DFT in solution

Excitonic Hamiltonian for the Fenna-Matthews-Olsen (FMO) complex

- FMO complex is involved in photosynthesis in green sulfur bacteria
  - Transmits electronic excitations (excitons) to antenna complexes
  - Trimeric structure with 7 bacteriochlorophyll (BChla) per monomer
- Cole et al. parameterized the FMO excitonic Hamiltonian
  - Used ONETEP calculations on each BChla site with implicit solvent

\[ \hat{H} = \sum_i \varepsilon_i |i\rangle \langle i| + \sum_{i \neq j} J_{ij} |i\rangle \langle j| \]

Site energies
(differences in orbital energies)

Good agreement with site energies “fit to reproduce experimental spectra”

A realistic electrostatic environment is vital!

Example 1944-atom cluster

- Pigment of interest
- All residues and pigments within 15 Å
- Implicit solvent
  - \( \varepsilon_\infty = 20 \) to represent low T solvent

Figs. 1 [cropped] & 2 from “Toward Ab Initio Optical Spectroscopy of the Fenna–Matthews–Olson Complex”.
Closing remarks

Large-scale DFT in solution: *Just add implicit solvent*

1. **Computationally inexpensive modelling of solvent effects**
   - Avoid costly explicit solvent
   - Can be accurate, despite apparent simplicity
   - Well-suited for linear-scaling DFT

2. **Without a solvent model, unphysical behaviour may be observed**
   - Vanishing HOMO-LUMO gaps
   - Spurious surface states
   - Realistic electrostatic environment is vital for large scale DFT

3. **Minimal parameter implicit solvation model**
   - Accurate free energies of solvation with only 2 parameters
   - Built on a general purpose Poisson solver library (DL_MG)
   - Open and periodic BCs (mixed BCs in future)
   - Currently available in ONETEP  

CASTEP coming soon!
Future prospects

Free energies of binding$^1$

Energy Decomposition Analysis (EDA)$^2$

Drug design

Organic photovoltaics

Dyes

TDDFT$^3$

Explicit + implicit solvent$^3$

Colour prediction

Solid electrolyte interphase (SEI)

Ionic solutions

Battery chemistry


Image of Nissan Leaf at the 2009 Tokyo motor show by Tennen-Gas (Own work) [CC BY-SA 3.0], via Wikimedia Commons
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ARCHER eCSE project collaborators

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- Phil Hasnip (York, CASTEP)

Previous work on solvent model

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- Mike C. Payne
- Jacek Dziedzic
- Chris-Kriton Skylaris
- Lucian Anton

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Thank you for your attention.
ONETEP

www.onetep.org

Introducing ONETEP: Linear-scaling density functional simulations on parallel computers

DL_MG
ccpforge.cse.rl.ac.uk

DL_MG: A parallel multigrid Poisson and Poisson-Boltzmann solver for electronic structure calculations in vacuum and solution

HECToR dCSE and ARCHER eCSE projects

dCSE: Multigrid solver module for ONETEP, CASTEP and other codes

eCSE01-004: A pinch of salt in ONETEP’s solvent model

eCSE07-006: Implementation and optimisation of advanced functionality in CASTEP and ONETEP

Minimal Parameter implicit Solvent Model (MPSM)

Minimal parameter implicit solvent model for ab initio electronic-structure calculations

Large-scale DFT calculations in implicit solvent—A case study on the T4 lysozyme L99A/M102Q protein
Appendix: Free energy of solvation

What do we mean by “solvation”? 

- Change in internal energy due to the environment is not the full story: 
  - Physically meaningful results must account for entropy, temperature. 
  - These are included in the thermodynamic free energy. 
- We are typically interested in the “free energy of solvation” 
  - “the reversible work required to transfer the solute in a fixed configuration from vacuum to solution”

$$\Delta G_{\text{sol}} = \Delta G_{\text{es}} + \Delta G_{\text{non-es}}$$

Electrostatic 
- Interaction of solute with dielectric medium

Non-electrostatic 
- Cost of creating cavity in solvent 
- Solute/solvent dispersion-repulsion interactions

Appendix: DL_MG implementation

Solve GPE using a defect-corrected multigrid solver (DL_MG)\textsuperscript{1,2}

\[ \hat{A}_2^h \phi^{(0)} = f \]

2\textsuperscript{nd}-order solution

\[ \hat{A}_d^h \phi^{(i)} = f - \hat{A}_d^h \phi^{(i)} \]

High-order defect correction

\[ \hat{A}_2^h e_{2,d}^{(i)} = r_d^{(i)} \]

\[ \phi^{(i+1)} = \phi^{(i)} + e_{2,d}^{(i)} \]

1. Efficient real-space solution to second-order using multigrid
2. Highly parallelised: MPI + OpenMP
3. Input and output on real-space Cartesian grid
4. Higher-order accuracy obtained by defect correction approach.\textsuperscript{1,2,3}

\[ \hat{A} = \nabla \cdot \varepsilon \nabla \]

\[ f = -4\pi n \]

\[ e^{(i)} = \phi - \phi^{(i)} \]

\[ |\phi^{(i)} - \phi^{(i+1)}| < \max(\tau_{\phi}^{\text{abs}}, \tau_{\phi}^{\text{rel}}) |\phi^{(i)}| \]

\[ |r_d^{(i+1)}| < \max(\tau_{r_d}^{\text{abs}}, \tau_{r_d}^{\text{rel}}) |r_d^{(0)}| \]

ONETEP

\[ \phi(n) \]

Improved solution

Appendix: MPSM implementation

Coarse-grained boundary conditions

- Evaluation of BC integral is computationally costly
- Replace integral with sum over point charges
- Point charges represent summed charge of block of space
- Assumes homogeneous dielectric permittivity for entire cell
- Significant reduces prefactor with negligible error penalty

\[
\phi_{\text{es}}(\mathbf{r}) = \frac{1}{\varepsilon_{\infty}} \int_{\Omega} d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
\]

Coarse graining

\[
\phi_{\text{es}}^{\text{CG}}(\mathbf{r}) \approx \frac{1}{\varepsilon_{\infty}} \sum_{i}^{N_{CG}} \frac{n_{\text{tot}}^{\text{CG}}(\mathbf{R}_i)}{|\mathbf{r} - \mathbf{R}_i|}
\]

Smeared ionic cores

- Represent ionic core charge with Gaussians
- Solve NPE for total molecular charge density
- Avoids numerical issues with point-charges
- Single width parameter, \(\sigma\)

\[
E_{\text{es}}[n_{\text{tot}}] = \frac{1}{2} \int d\mathbf{r} n_{\text{tot}}(\mathbf{r}) \phi_{\text{es}}[n_{\text{tot}}](\mathbf{r})
\]

\[
n_{\text{elec}}(\mathbf{r}) + n_{\text{si}}(\mathbf{r})
\]

\[
n_{I}(\mathbf{r}) = -\frac{Z_I}{(\sigma \pi^{1/2})^3} \exp\left(-\frac{|\mathbf{r} - \mathbf{R}_I|^2}{\sigma^2}\right)
\]

\[
n_{\text{si}}(\mathbf{r}) = \sum_{I} n_{I}(\mathbf{r})
\]

Appendix: Recent DL_MG developments

A flexible, scalable multigrid Poisson solver library

- High-order defect correction integrated into library
- Vital to reduce error in computed energies
- Demonstrated efficient scaling
  - Up to \(\sim 10^9\) grid points
  - 10s to 100s of processors

Solving the GPE for a synthetic test system: \texttt{erf\_eps}\(^2\)

Solving the SPE for a graphene sheet

- ONETEP with DL_MG
- 448 atom periodic sheet
- PBE XC functional
- Norm-conserving PSPs
- \(256 \times 264 \times 240\) grid
- Error wrt analytic solution

\[
\nabla^2 \phi(\mathbf{r}) = -4\pi n(\mathbf{r})
\]

\[
\phi(\mathbf{r}) = \left(\frac{1}{2\pi\sigma^2}\right)^{3/2} \exp\left(\frac{-|\mathbf{r} - \mathbf{R}|^2}{2\sigma^2}\right)
\]

\[
\varepsilon(\mathbf{r}) = 1 + \frac{(\varepsilon_\infty - 1)}{2} \left[1 + \left(\frac{|\mathbf{r} - \mathbf{R} - d_0|}{\Delta}\right)^2\right]
\]

Analytic \(n(\mathbf{r})\) can be derived

\[
\sigma = 0.5 a_0, d_0 = 1.7 a_0, \Delta = 0.3 a_0, \varepsilon_\infty = 78.36, R = (5 a_0, 5 a_0, 5 a_0)
\]

Graphene calculations performed on ARCHER, “erf\_eps” calculations performed on EPSRC MMM Hub “Thomas”.

Appendix: Periodic BC results

Periodic boundary condition (BC) solvation
- Only full open BC solvation available previously in ONETEP MPSM
  - Full periodic BC solvation now available
  - Stepping stone to mixed open/periodic BC solvation

Free energy of solvation, $\Delta G_{\text{sol}}$ “the reversible work required to transfer the solute in a fixed configuration from vacuum to solution”

\[
E_{\text{es}}[n_{\text{tot}}] = \frac{1}{2} \int \text{d}r \ n_{\text{tot}}(r) \phi[n_{\text{tot}}](r) \\
+ (E_{\text{locps}}[n_{\text{elec}}] - E_{\text{si-elec}}[n_{\text{elec}}]) \\
+ (E_{\text{ion-ion}} - E_{\text{si-si}})
\]

BCs must be consistently treated in each term!

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Charge</th>
<th>Free energy of solvation</th>
<th>OBC$^a$</th>
<th>PBC$^a$</th>
<th>PBC$^b$</th>
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<tbody>
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<td>-72.386</td>
<td>-49.952</td>
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</tr>
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</table>

$^a$Molecule located at the centre of the simulation cell.
$^b$Molecule located at the origin of the simulation cell.

- Solvation in H$_2$O (kcal/mol)
- PBE XC functional
- Norm-conserving PSPs
- 800 eV KE cutoff
- Fixed dielectric cavity

Appendix: CASTEP implementation

Implicit solvation and open BCs for the CASTEP\textsuperscript{1} community
• Implicit solvent and open BC electrostatics not previously available
  - Full open BC MPSM implemented in CASTEP
  - Open BC electrostatics in vacuum as a bonus!

Many components, e.g.
• DL\_MG library interface
• Open BC local pseudopotential
• Open BC ion-ion interaction
• Smear ion representation
• Non-electrostatic contribution

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Charge</th>
<th>Free energy of solvation / kcal/mol</th>
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<td>1</td>
<td>-72.666</td>
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<td>-72.666</td>
</tr>
</tbody>
</table>

Some shared features with ONETEP
\textit{BUT} also substantial differences, e.g.
Satisfying MG grid size constraints

Solvation in $\text{H}_2\text{O}$ with open BCs
• PBE exchange-correlation
• Norm-conserving pseudopotentials
• Fixed dielectric cavity
• KE cutoff set for identical fine grid sizes
• $150^3$ fine grid
  - Padded to $161^3$ for CASTEP
  - Truncated to $145^3$ for ONETEP