Direct and Simple Experimental Method to Calculate Partial Charges with Atomistic Correspondence to ab – initio Methods

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Background

Derivation of partial charges in small and large scale molecular systems is important for modeling of various experimental and theoretical properties like dipole moments, auto-correlation functions, charge disparity, understanding of dispersion, benchmark of classical MD simulations and electrostatic potential energy surface mapping. A correspondence between theoretical calculations (based on single/small number of molecules) is usually established with macroscopic IR/Raman spectra or dipole moment measurements. Such comparisons are indirect and lack a fine mapping of electrostatic potential from theory to experiment. In a new approach developed as the experimental part of this work, partial charges are calculated from crystallographic model refinement. The experimental method exhibits a satisfactory correspondence with partial charges obtained using quantum chemistry calculations. gas phase partial charges from CHELPG method and condensed phase Löwdin charges correlate well and validate this experimental method.

Objectives

- A simple method to derive partial charges for small organic molecules from their single-crystal structure.
- Understanding correlation of atomistic charges derived from experiments to theoretical methods in gas and condensed phase.
- Partial atomic charges for gas phase geometries using methods like **CH**arges from **E**lectrostatic **P**otential **G**rid (CHELPG), natural bond orbital analysis[1].
- Plane-wave periodic DFT using PBE projector augmented-wave-based pseudopotentials to derive Löwdin charges in the condensed phase[2].
- Development of force-fields, dipole moments using these correlations.

Experimental and Theoretical Details

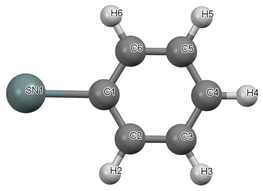
- Samples were taken on a Bruker KAPPA APEX II DUO with a molybdenum radiation source and equipped with a CCD area detector. COSMO (Bruker AXS) was used for strategy determination. SAINT (Bruker AXS) was used for integration and refinement. SADABS (AXS) was used for scaling and absorption correction. XPREP (Sheldrick) was used to determine the space group. XL (Sheldrick, 2008) was used for computing structure refinement and XS (Sheldrick, 2008) was used for computing the structure solution[3].
- Partial charges were calculated using atomic occupancies obtained from experiments.
- For gas phase charges, a single molecular unit from single-crystal XRD unit cell was extracted for geometry optimization and partial charge derivation.
- For plane-wave periodic DFT calculations, a unit cell was used to derive SCF, optimized and variable-cell optimizations to derive Löwdin charges.
- Higher k-mesh (depending upon the unit cell dimensions in each case) were used for final SCF calculations to derive charges.
- Since CHELPG scheme uses a vdW radius for atoms to compute partial charges via fitting them to electrostatic potential, a variational value of radii for Sn atom was used from 1.6 Å to 1.9 Å. Results for r(Sn) = 1.7 Å and 1.8 Å are used here for comparison with experiments.
- For MP2 derived charges on optimized geometries, B3LYP was used for optimization.
- Effective core potential was used for Sn atom, while People's basis was used for other atoms with polarized and diffused functions.

Results

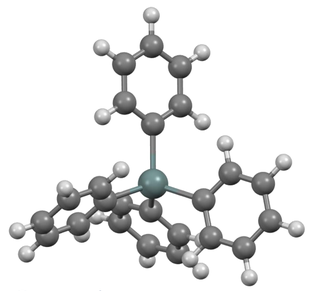
Case 1. Tetraphenyl tin

a = 12.0052 Å, b = 12.0052 Å, c = 6.4372 Å

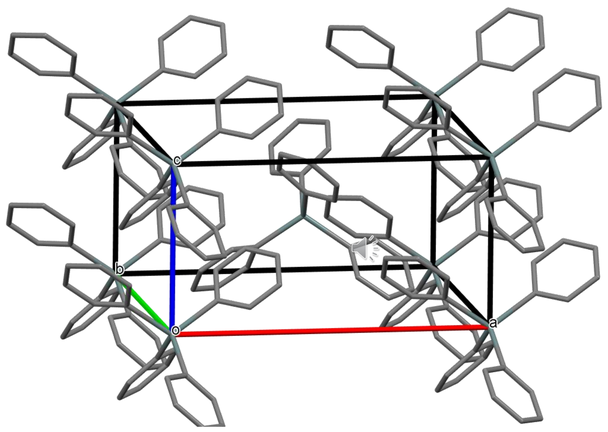
α = β = γ = 90°



An asymmetric unit of Tetraphenyl tin showing atom name scheme



Gas phase geometry used for quantum calculations



Packing in a unit cell, Sn atom occupies the center and the edges

Charges from gas phase calculations:

	Charges						
Atoms	**Exp1**	**Exp2**	**Exp3**	**Theor1**	**Theor2**	**Theor3**	**Theor4**
Sn1	1.441333	1.363822	1.157231	1.224003	1.106202	1.261736	1.087364
C1	-0.24474	-0.2846	-0.29011	-0.40299	-0.34965	-0.40884	-0.33019
C2	-0.06904	-0.07438	0.000501	0.072537	0.045861	0.210764	0.166374
H2	0.052578	0.084923	0.013618	-0.14826	-0.14289	-0.22142	-0.2111
C3	-0.10562	-0.11574	-0.00773	-0.04991	-0.05224	-0.0504	-0.05408
H3	0.060938	0.064113	0.005268	-0.15514	-0.15543	-0.12777	-0.12731
C4	-0.05722	-0.08541	0.049485	0.055613	0.039565	-0.0102	-0.0353
H4	0.039693	0.079153	-0.00799	-0.00702	0.003592	-0.05303	-0.03634
C5	-0.11651	-0.09873	-0.08024	0.107856	0.107138	0.124587	0.123219
H5	0.021599	0.044253	-0.00432	0.086411	0.087079	0.090138	0.091113
C6	-0.00888	-0.02122	0.037254	0.100281	0.101565	0.107094	0.107949
H6	0.066868	0.066666	-0.00511	0.034615	0.03886	0.023638	0.033814

Exp1-4 are various data sets obtained by varying refinement/structural constraints/ thermal schemes. These are in detailed discussed in poster PS2-7 by Taylor Keller et. al. from our group.

Theor1: MP2/ECP&6-31++G* SCF with r(Sn) = 1.7 Å

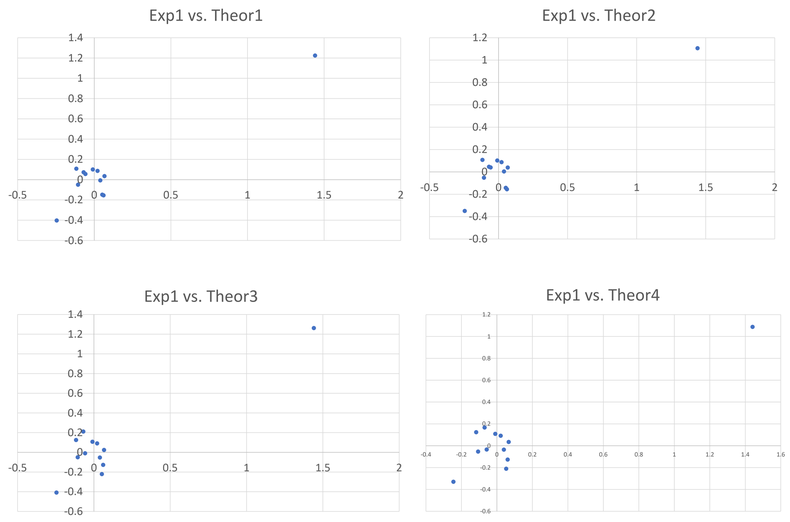
Theor2: MP2/ECP&6-31++G* SCF with r(Sn) = 1.8 Å

Theor3: B3LYP//MP2/ECP&6-31++G* Opt. with r(Sn) = 1.7 Å.

Theor4: B3LYP//MP2/ECP&6-31++G* Opt. with r(Sn) = 1.8 Å.

Results

Correlation plots



Condensed phase charges obtained from pwdft calculations:

- PWDFT predicts a Löwdin charge of 1.08 on Sn atom and charge on C1 to be - 0.22.
- It fails to predict accurate charges for light H atoms and also nature of polarization on ortho C atoms.
- Since these charges from SCF only, a detailed analysis of relaxed and variable cell relaxed geometry is required.

Conclusions and Future

- A simple method is presented here to extract reliable atomic partial charges using single-crystal XRD data.
- For heavy atoms like Tin, the agreement is good.
- For light atoms like H, more accurate modeling is required.
- Solid state charges from plane-wave DFT which can provide better anisotropic charge distributions and includes effect of intermolecular interactions will be used in next set of calculations.

Acknowledgements

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