

Algorithms for Electronic Structure Calculations in Real Space

Charles Lena, N. Scott Bobbitt, Grady Schofield, James R. Chelikowsky
University of Texas at Austin



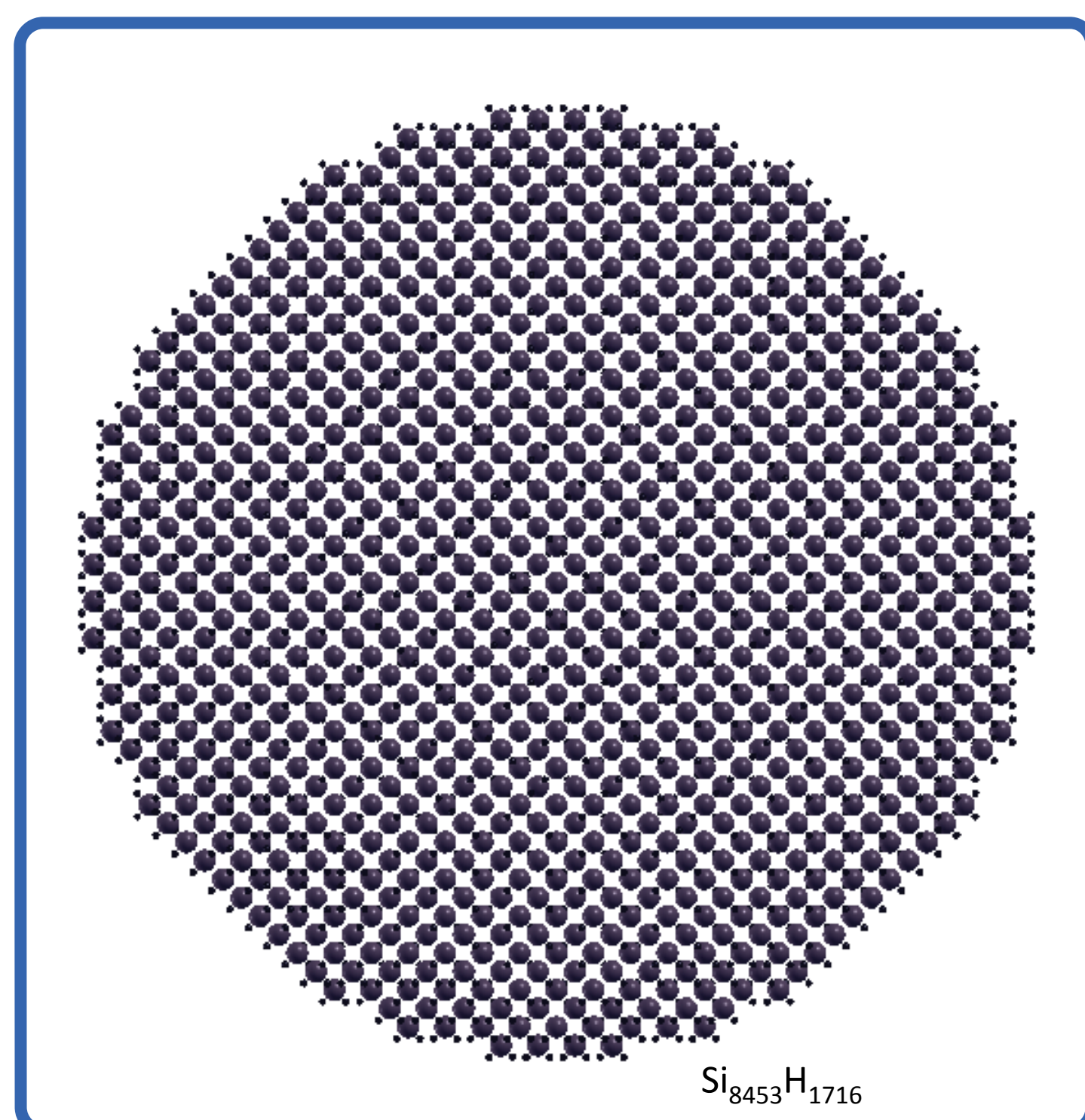
Large Scale Ground State Calculations

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + V_{ion}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r}) \right] \psi_n(\vec{r}) = E_n \psi_n(\vec{r})$$

Goals: Provide fast and accurate *ab initio* computational methods for designing and predicting new energy related materials. We want to reliably apply a massively parallel treatment of pseudopotential-density functional theory to complex systems in the 100,000+ atom range.

Utilizing massively parallel computers at NERSC, we can now handle systems with over 10,000 atoms employing algorithms based on subspace filtering [1].

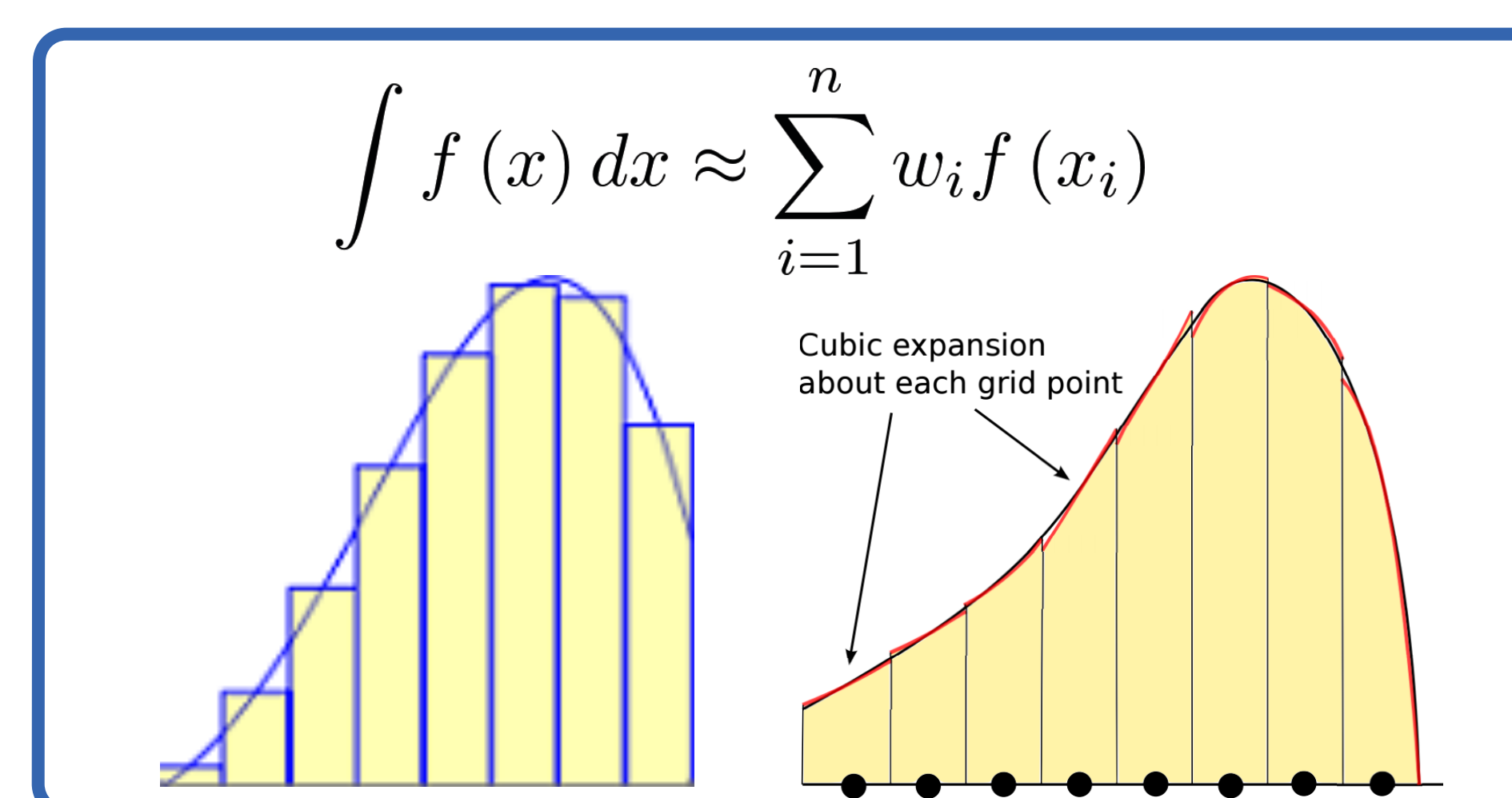
Example shown here: Large silicon nanocrystal passivated with hydrogen atoms. The nanocrystal density of state has converged to that expected for a bulk crystal.



High Order Force Calculations

Atomic forces require a finer grid spacing than total energy calculations. The cost of the computation increases roughly as the cube of the grid spacing.

We apply an improved integration technique to the force calculation and demonstrate that we can calculate accurate, converged forces using a coarser grid spacing with this new technique [2].



The wave function is approximated on intermediate points by several high order Taylor series.

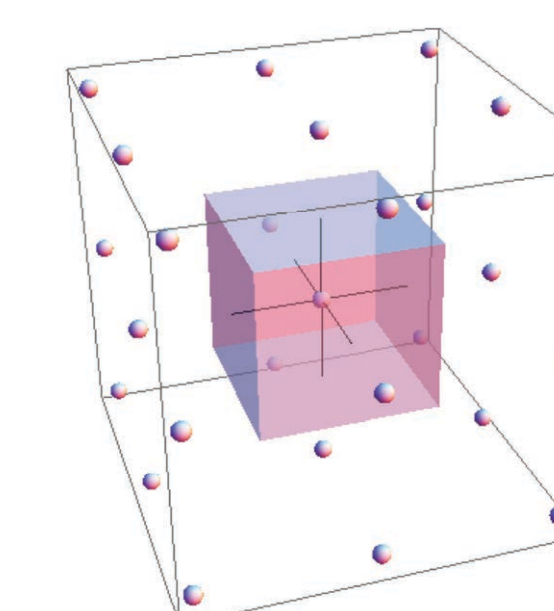
Combining with a finite difference scheme provides a smooth approximation of the wave function.

A 20 point Gaussian quadrature rule is applied for the integration.

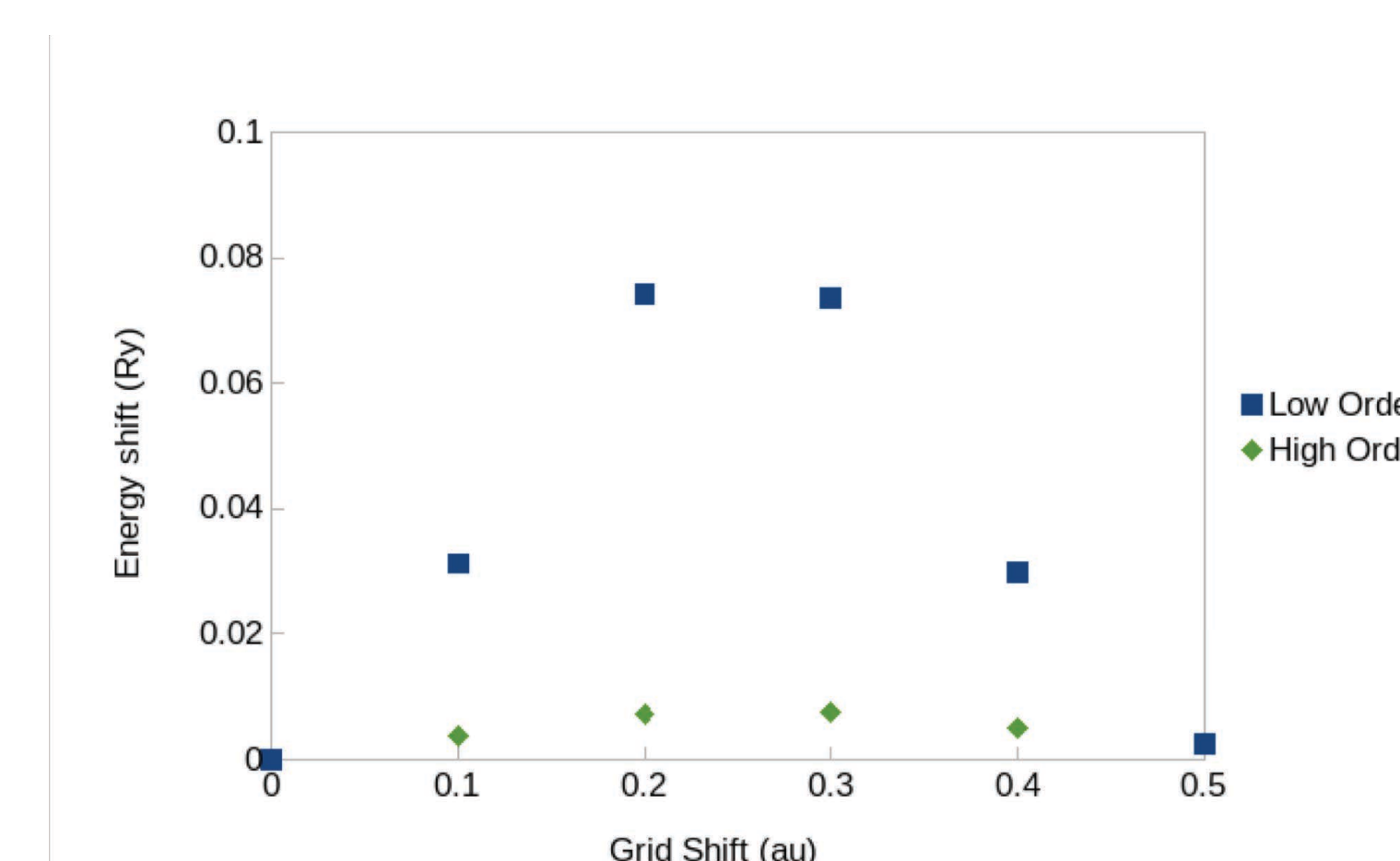
$$F = \sum_{i \neq j} \frac{Z_i Z_j}{R^2} + \int \rho(\mathbf{r}) \frac{dV_n(r-R)}{dR}$$

$$\int f(\psi) d^3r \approx \psi(r) h^3$$

Integration was originally done with a Riemann sum of cubes at each grid point.



Improving Integration: Impact

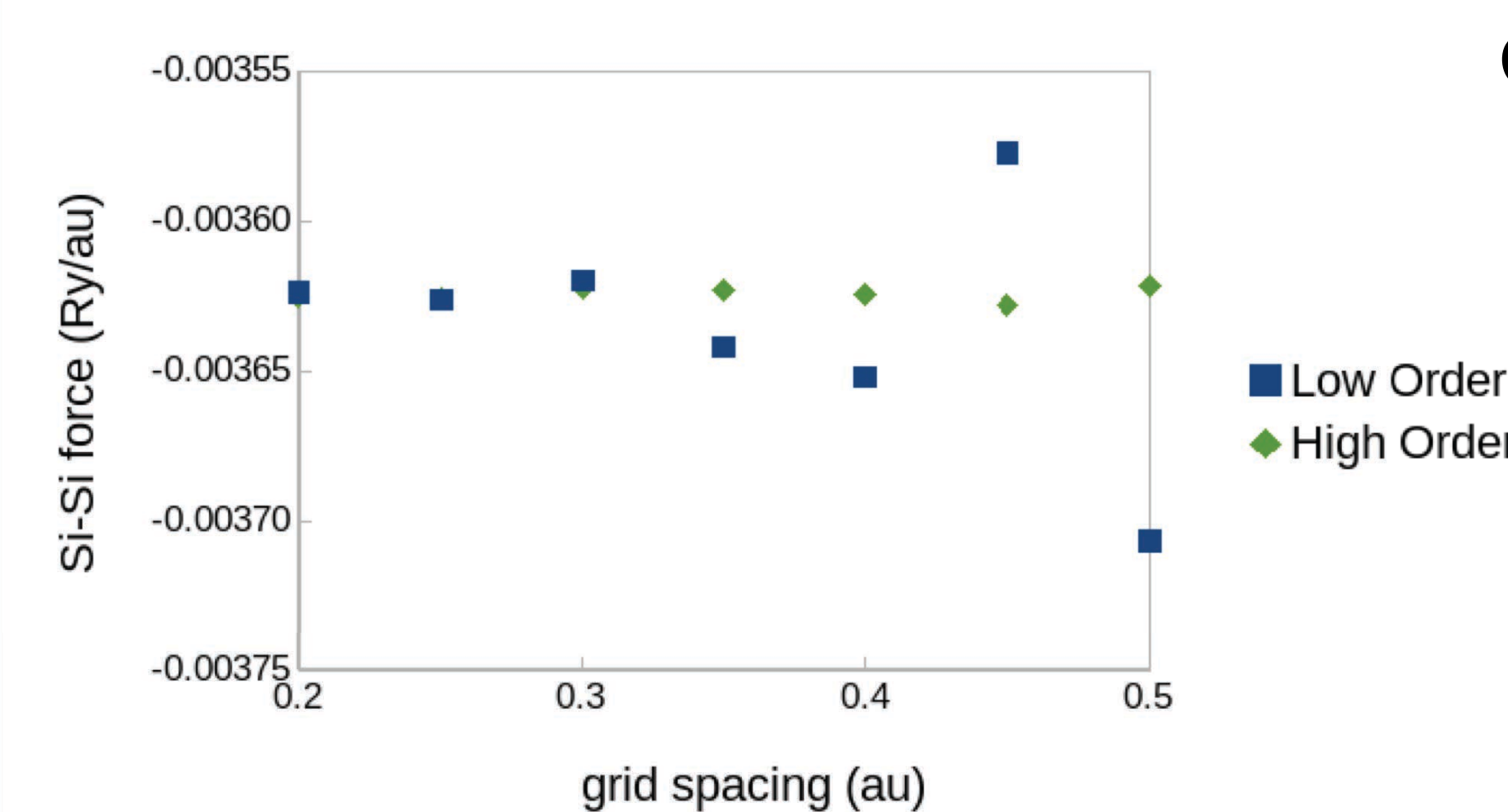


Left: The improved integration scheme reduces variations in energy as a benzene molecule is translated through space.

Right: Vibrational frequencies for CO₂. The high order result attains comparable accuracy as the low order result, but uses a much coarser grid.

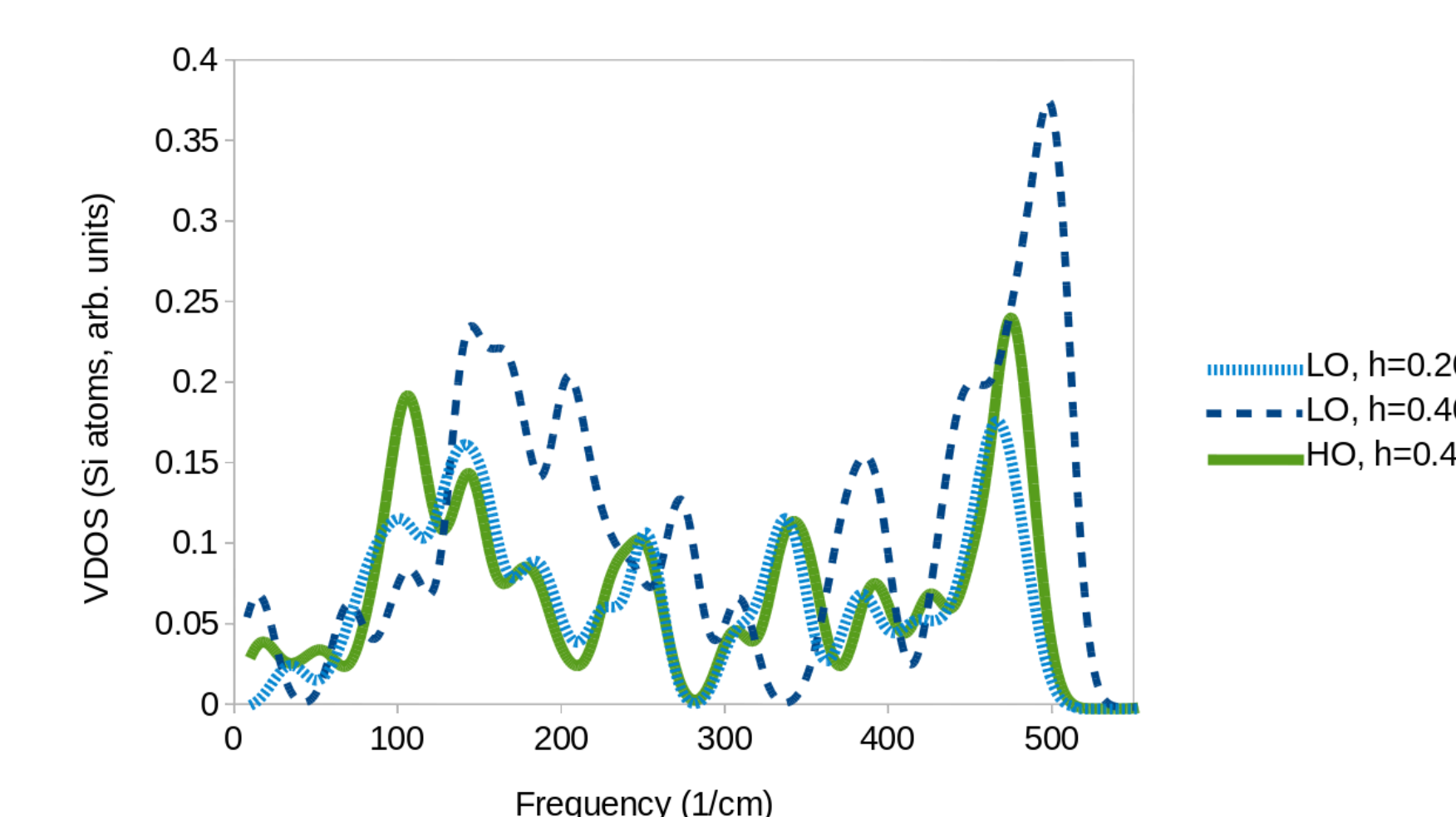
Low Order	Low Order	High Order	Exp.[Ref.3]
<i>h</i> =0.15	<i>h</i> =0.30	<i>h</i> =0.30	
2415	2301	2400	2349
1346	1517	1335	1333
642	603	628	667
641	603	628	667

Units in a.u., cm⁻¹



The force between two Si atoms in a cluster as a function of grid spacing. With the high order integration scheme, the force is converged up to grid spacing with $h = 0.50$, while low order results diverge at $h = 0.35$.

Computational Savings



Using the high order scheme, we can compute the vibrational spectrum of Si₃₅H₃₆ using a grid spacing of $h = 0.40$ instead of $h = 0.20$ with the low order scheme.

References

- 1.Y. Zhou, Y. Saad, M.L. Tiago, J.R. Chelikowsky, Phys. Rev. E. 74, 2006; G. Schofield, J.R. Chelikowsky, Y. Saad, Comp. Phys. Comm. 183, 497 (2012).
- 2.N. S. Bobbitt, G. Schofield, C. Lena, J. R. Chelikowsky, Physical Chemistry Chemical Physics, 2015, DOI: 10.1039/C5CP02561C
- 3.T. Shimanouchi. Tables of molecular vibrational frequencies consolidated. volume I. Technical report, DTIC Document, 1972

Acknowledgments

We wish to acknowledge support provided by the Scientific Discovery through Advanced Computing (SciDAC) program funded by U.S. Department of Energy, Office of Science Advanced Scientific Computing Research and Basic Energy Sciences under award number DESC0008877. This research used resources of the National Energy Research Scientific Computing Center