Computations of Properties of Atoms and Molecules Using Relativistic Coupled Cluster Theory

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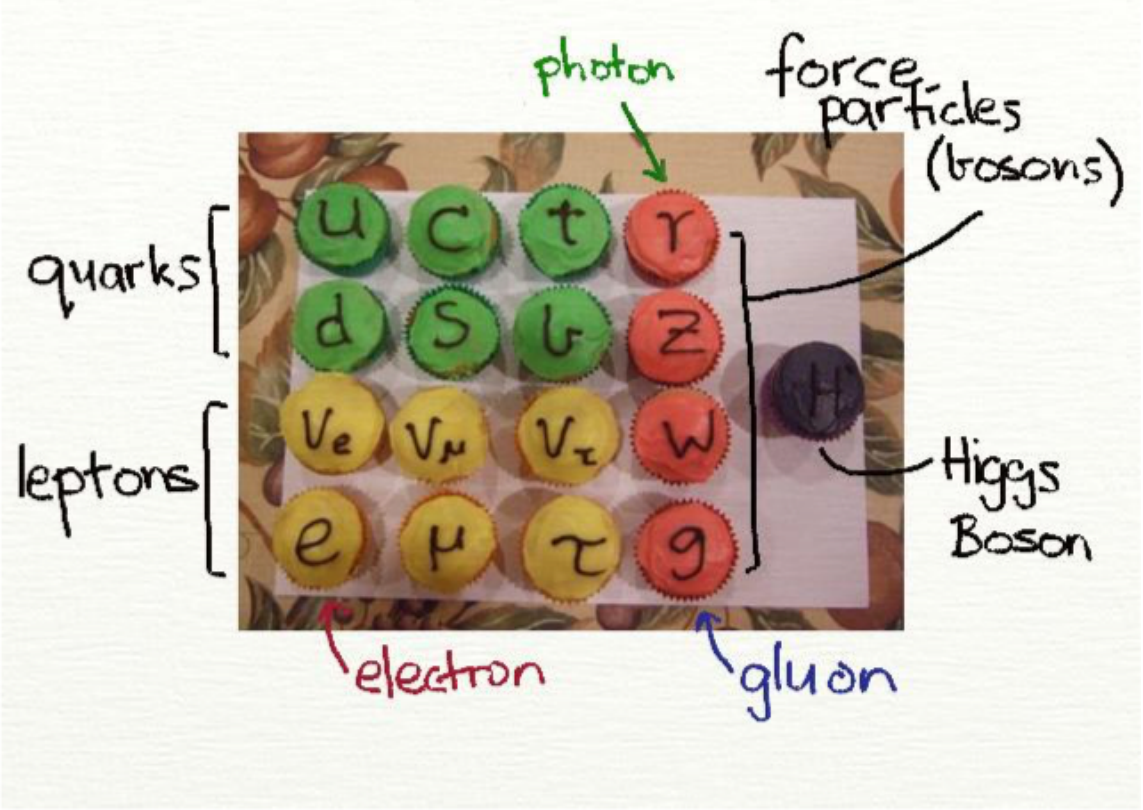
Outline

- The Standard Model of Particle Physics and Beyond.
- Probing Physics Beyond Standard Model using Atoms and Molecules.
- Relativistic Hartree-Fock and Coupled Cluster Equations.
- The Importance of Parallel Computing in Relativistic Atomic and Molecular Calculations.
- Results.
- Conclusions.

Standard Model of Particle Physics

Six quarks and six leptons are the basic building blocks of matter

Quantum theory of strong, electromagnetic and weak forces with the latter two unified



The Standard Model is incomplete!

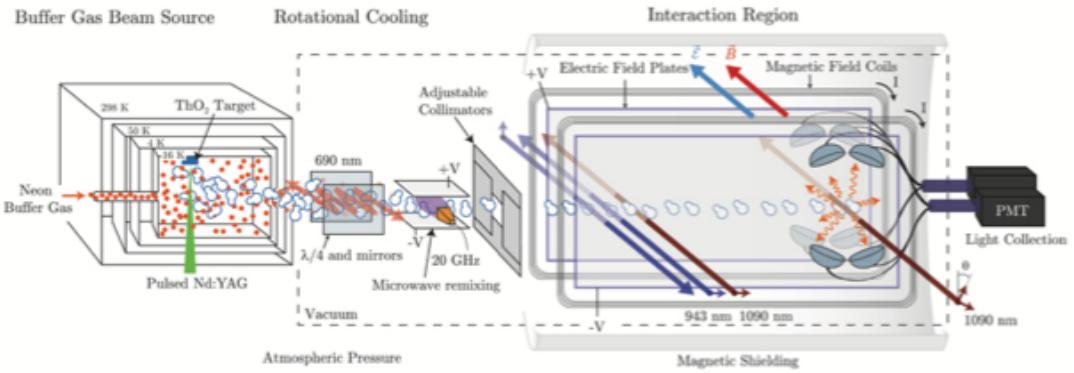
Image courtesy: https://www.quantumdiaries.org/2014/12/01/standard-model-introduction/

Beyond the Standard Model

- Two ways of probing physics beyond the Standard Model:

Accelerators (high energy probes).
Example: LHC.

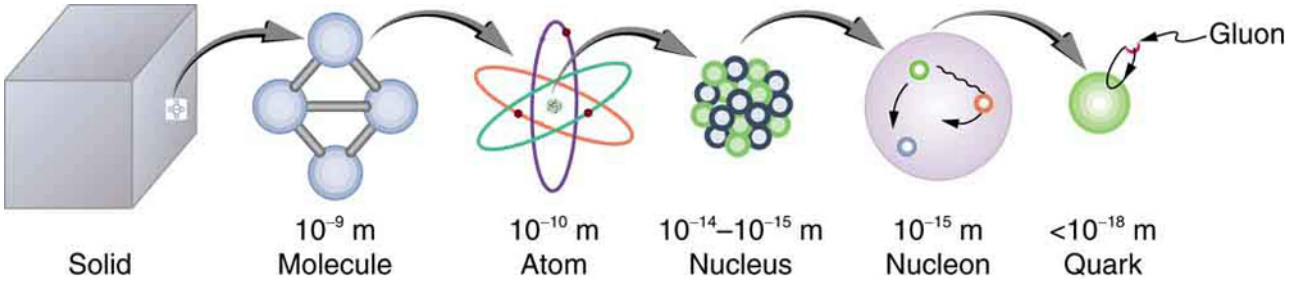
Non-accelerator approach (low energies).
But high precision.



Can probe energy scales larger than LHC!

Image courtesy: https://www.forbes.com/sites/startswithabang/2016/03/22/what-it-means-if-cern-discovers-a-new-particle/
http://www.danielang.net/2016/10/16/guide-to-the-acme-edm-experiment-a-simple-overview/

Using Atoms and Molecules to Probe Fundamental Physics



We can use atoms and molecules to probe fundamental physics, at the level of electrons and quarks!!

Atoms and Molecules follow the laws of quantum mechanics.

$H\psi = E\psi$

Ψ is called the wavefunction. It is a probability amplitude. We solve for this quantity in our calculations.

Unfortunately, exact solutions only for H and H_2^+.

We use quantum many-body methods to a certain level of approximation to handle every other atom/molecule, to obtain ψ.

All properties can be obtained from ψ.

Image courtesy: https://opentextbc.ca/physicstestbook2/chapter/introduction-to-particle-physics/

Wavefunctions of Atoms and Molecules

- The current gold standard for the relativistic theory of atoms and molecules is the relativistic coupled cluster theoy.
- In this theory, which combines the special theory of relativity and quantum mechanics, the wavefunction is given by: $\psi = e^{T} \Phi$
- Φ is the DF wavefunction, and it is based on the independent particle model.
- We first solve for the Dirac-Fock (DF) wavefunction, followed by the more accurate relativistic coupled cluster (RCC) wavefunction.
- We then compute properties of interest to us.

$$\bar{O} = \int \psi^{*} O \psi d^{3}r$$

Computation of DF Wavefunction: HPC Aspects

$\Phi_0 = \det\{\phi_1\phi_2\ldots\phi_N\}$ We solve for the single particle wavefunctions, or orbitals.
These orbitals are 4-component structures. They can be treated as having 2 components.

$$\boldsymbol{t}(\mathbf{1})\varphi_c(1) + \sum_b \int_{r_2} \varphi_b^*(2)\frac{e^2}{r_{12}}\varphi_b(2)d^3\vec{r}_2\varphi_c(1) - \sum_b \int_{r_2} \varphi_b^*(2)\frac{e^2}{r_{12}}\varphi_c(2)d^3\vec{r}_2\varphi_b(1) = \epsilon_c\varphi_c$$

t : kinetic energy plus electron-nucleus Interaction.

Integro-differential equations.
Can be solved by a linear algebraic approach.
Basis sets: $\phi^L_i = \Sigma_i C_{in} \chi^L_n$
$\phi^S_i = \Sigma_i C_{in} \chi^S_n$

Matrix form of DF equations: **FC = ESC** This can be rewritten in the form: **F'C'=EC'**

The equations are solved self consistently, till convergence. F' is made of one and two electron integrals. They are of the forms: LL, SS, and LS, for the one electron integrals, and LLLL, SSSS, and LLSS, for the two electron integrals.

These integrals are the most time consuming part of the computations. The calculations of these quantities are parallelized, using MPI (developed at the Univ of Tokyo, and parallelized by our collaborators, at Tokyo Metropolitan University).

DF results

We test the parallel code for SrF (a medium size basis):
For the molecular properties associated with the electric dipole moment of the molecule, and molecule's permanent electric dipole moment itself. We choose SrF, since is heavy enough that relativistic effects become important, but not too heavy that it takes too much computational time. Also, SrF is a useful molecule for tests of fundamental physics.

Dirac-Fock results on the cluster at IIA, Bengaluru, India:
CPU: dual Xeon X5675, 2 sockets and 12 cores (6 per socket) per node, 3.06 GHz clock speed, 3.46 GHz Turbo, 6.4GT/s. Memory: 96 GB per node.
Compilers: ICC Version 12.0.5.220 , IFORT Version 12.0.5.220.
Libraries: mvapich 1.2/ mvapich2 1.6, and Netlib LAPACK95 library provided UTChem.
Interconnect: Infiniband QDR 40 Gb/s.

DF results

Nodes	Cores	Time (hrs:mins)
1	1	24:00
1	2	9:30
1	4	5:50
1	6	4:44
1	8	4:00
1	10	3:45
1	12	3:36
2	6	3:32
3	6	3:35
4	6	3:31

The times given are for the solution of the DF equations, as well as the properties that we mentioned in the previous slides.

Computation of Atomic/Molecular RCC Wavefunction: HPC Aspects

$\Psi=(e^{T})\Phi$; $T=T_1+T_2+\ldots$

t amplitudes

$T_1 = \Sigma_{ia}\, t_{ia}\, E_{ia}$, and $T_2 = \Sigma_{ijab}\, t_{ijab}\, E_{ijab}$

Let T_1 and T_2 be the excitation operators associated with the inner electrons, and S_1 and S_2 with the outer ones. Then, the resulting RCC equations, in the RCCSD (relativistic coupled cluster singles and doubles approximation) are of the form:

$A(T^0)\, T^0 = B$
$A'(T^0)\, S^0 = B' + B''(S^0)$

$C(T^0)\, T^1 = D + D'(T^0)$
$C'(T^0)\, S^1 = D''(T^0, S^0) + D'''(T^0, T^1, S^0)$

These equations are solved, using the iterative Jacobi method. For Tl (81 electrons), A ,A', C, C' are of the order $10^7 X 10^7$.

$$x_i^{k+1} = (b_i - \Sigma_{j\neq i}\, a_{ij} x_j^{k})/a_{ii}$$

x refers to the t amplitudes.

The number of indices increase as we go to the right.

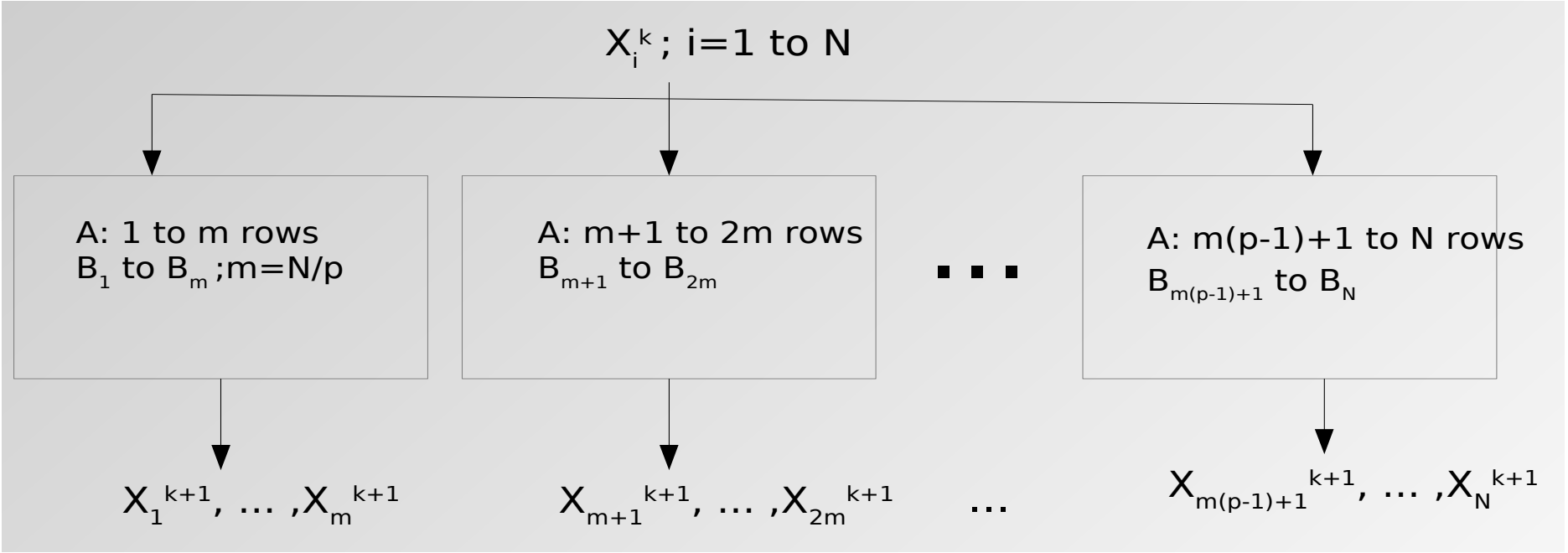
A property, O, is then: $O_{ia} + \Sigma_{ia}\, O_{ia} t_{ia} + \ldots + \Sigma_{ijabk}\, t_{ijab}\, t_{kajb}\, O_{ik} + \ldots$

The solution of the above equations and the computation of the matrix elements of A and the evaluation of O are obtained by parallelization (**MPI)**.

Computation of Atomic/Molecular RCC Wavefunction: HPC Aspects

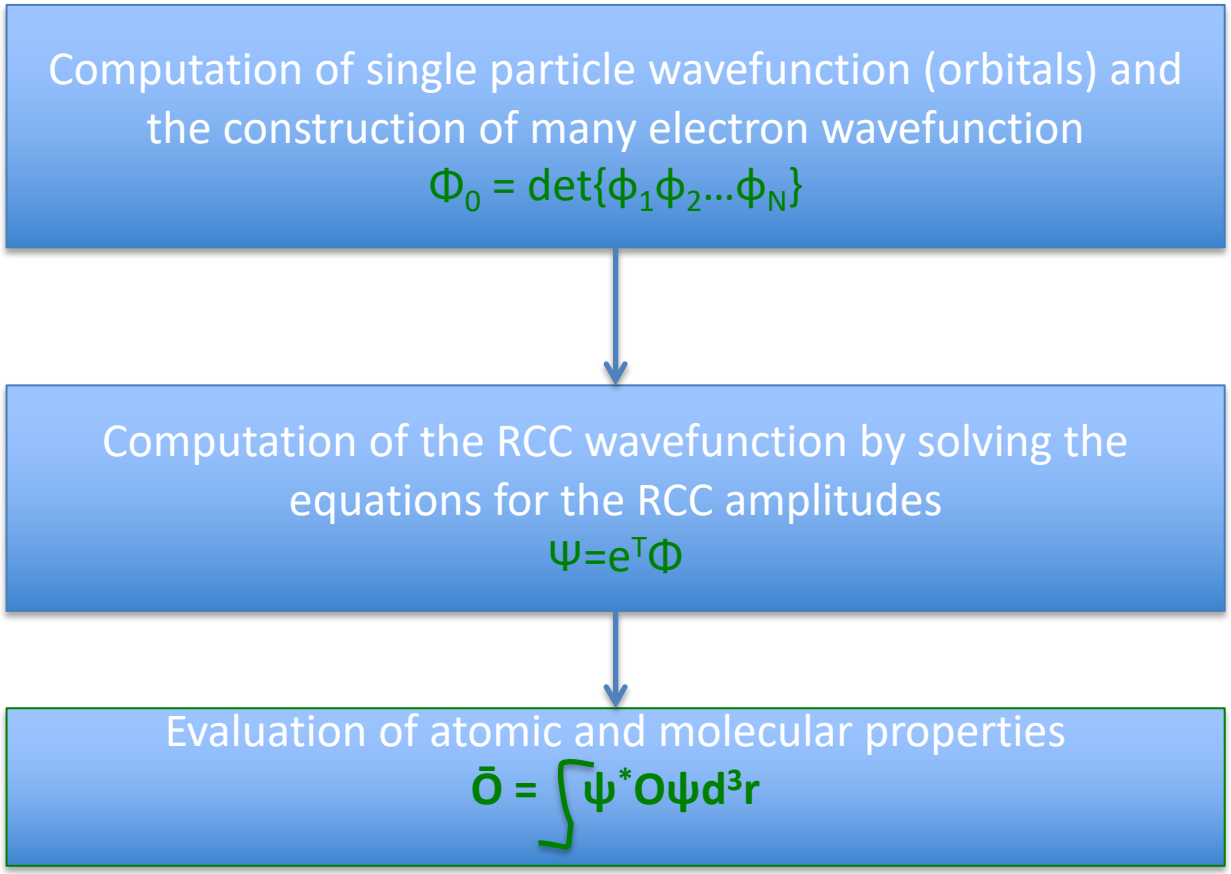
- Even after using the symmetry properties that reduce the computational cost, for an atom like Tl, the 2 electron integrals (which scales as N^4) take up about 6 GB (they enter the RCC equations via b_i), while A takes up 20-25 GB.
- The computations are, therefore, memory intensive.
- The compute intensive nature of the problem motivate us to parallelize the codes.

MPI Parallelization of RCC Equations



MPI_Send, MPI_Recv, and MPI_Bcast have been used.
The parallelization of A is very complex, as it contains several do loops.

A Summary of the Computation of Atomic and Molecular Properties



HPC techniques are needed for all three steps.

RCC results for Atoms

- The property, to explore proton and neutron EDMs, and thereby quark EDMs, is the nuclear Schiff Moment (NSM), which can probe Beyond the Standard Model physics, at the TeV scale.
- Using a non-terminating version of the RCC approach, we obtain a value of -1.77×10^{-17} $S/|e\ fm^3|$.
- This, when combined with experiment, gives us the upper bound on NSM: 4.18×10^{-13} $|e\ fm^3|$.

B K Sahoo and B P Das, J Phys B, RPMBT Conf Proc (2018)
Y Singh, B K Sahoo and B P Das, Phys Rev A Rap Comm (2014)
B K Sahoo and Ysingh, Phys Rev A Rap Comm (2015)

RCC results for Atoms: Scaling

For the Cs atom (basic RCC computation; more advanced calculations Will take weeks):

Nodes	Cores	Time (days)
1	1	15 days
1	10	6 days
1	20	4 days
2	20	4.5 days
3	30	3 days
4	40	2.5 days
5	50	2 days
6	60	1.5 days
7	70	1.3 days
8	80	1.2 days

RCC results for Molecules

- After ThO, YbF is the best candidate that has provided an upper bound on the electron electric dipole moment.
- The necessary theoretical input for setting the upper bound is the effective electric field, E_{eff}. It is like an internal field experienced by an electron, but much higher than lab fields (E_{eff} is of the order of GV/cm, while the highest lab fields are less than 100 kV/cm).
- The upper bound from the YbF experiment, in Imperial College, London, was 10.5×10^{-28} e cm.
- Our RCC calculations gave us an E_{eff} of 23.1 GV/cm, and improved the upper bound to 11.8×10^{-28} e cm (M Abe et al, PRA Rapid Comm, 2014).

RCC results for Molecules

- We also proposed mercury monohalides (HgX), as promising candidates for future electron EDM experiments.
- We found that they have extremely large E_{eff}, of over 100 GV/cm (VS Prasannaa et al, Phys Rev Lett, 2015)!
- This is about five times the E_{eff} of YbF.
- The electron EDM can probe new physics at the PeV (10^{15} eV) scale, which is well beyond the reach of current particle accelerators, and it can also provide insights into the matter-antimatter asymmetry in the Universe.

GPU Computing and Future Plans

- Plan to use GPUs in Tsubame 3.0, in collaboration with Prof. T Watanabe, GSIC, Tokyo Tech.
- Use ExaTensor (ADAC project), developed by D Lyakh, ORNL .
- ExaTensor is a software library for large-scale numerical tensor algebra on large-scale HPC platforms, including clusters, with applications in electronic structure simulations, quantum circuit simulations, etc.
- Will use ExaTensor to automatically generate the RCC equations, and solve them, using hybrid computing.

Conclusions

- HPC techniques are indispensable, for the calculations of atomic and molecular properties needed to probe new physics beyond the Standard Model of elementary particles.
- In particular, atomic and molecular theories using HPC methods, in combination with table top experiments have provided new limits for the electron and nuclear EDMs.
- HPC methods could play a even bigger role in the future by contributing to the improvement of the limits for the above two EDMs, and thereby testing the validity of supersymmetric theories and other extensions of the Standard Model, which predict Dark Matter and other profound cosmological phenomena.

THANK YOU!