Theorists Close In on Improved Atomic Property Predictions

January 13 2010

(PhysOrg.com) -- Scientists at the National Institute of Standards and Technology and Indiana University have determined the most accurate values ever for a fundamental property of the element lithium using a novel approach that may permit scientists to do the same for other atoms in the periodic table.

NIST's James Sims and IU's Stanley Hagstrom have calculated four excitation energies for the lithium atom approximately 100 times more accurately than any previous calculations or experimental measurements. Precise determination of excitation energy—the amount necessary to raise an atom from a base energy level to the next higher—has intrinsic value for fundamental research into atomic behavior, but the success of the method the team employed has implications that go beyond lithium alone.

The theorists have overcome major computational and conceptual hurdles that for decades have prevented scientists from using quantum mechanics to predict electron excitation energies from first principles. Sims first proposed in the late 1960s that such a quantum approach could be possible, but its application to anything more than two electrons required a fiendishly difficult set of calculations that, until recently, was beyond the capacity of even the world's fastest computers. In 2006 the team used a novel combination of algorithms, extended precision computing and the increase in power brought about by parallel computing to calculate the most accurate values ever for a simple, two-electron hydrogen molecule.

By making improvements to those algorithms, Sims and Hagstrom now have been able to apply their approach to the significantly more difficult problem of lithium, which has three electrons. Much of the original difficulty with their method stems from the fact that in atoms with more than one electron the mutually repulsive forces among these tiny elementary particles introduces complications that make calculations extremely time-consuming, if not practically impossible.

Sims says that while the lithium calculation is valuable in itself, the deeper import of refining their method is that it should enable the calculation of excitation energies for beryllium, which has four electrons. In turn, this next achievement should enable theorists to predict with greater accuracy values for all of the remaining elements in the second row of the periodic table, from beryllium to neon, and potentially the rest of the periodic table as well. “The mathematical troubles we have with multiple electrons can all be reduced to problems with four electrons,” says Sims, a quantum chemist in the mathematics and computational sciences division. “Once we’ve tackled that, the mathematics for other elements is not any more difficult inherently—there’s just more number-crunching involved.”

To obtain their results, the researchers used 32 parallel processors in a NIST computer cluster, where they are currently working on the calculations for beryllium.

High precision determinations of excitation energies are of interest to scientists and engineers who characterize and model all types of gaseous systems, including plasmas and planetary atmospheres. Other application areas include astrophysics and health physics.

More information: J.S. Sims and S.A. Hagstrom. Hylleraas-configuration-interaction study of the 2 2S ground state of neutral lithium and the first five excited 2S states. Physical Review A, Nov. 19

2009, DOI:10.1103/PhysRevA.80.052507