

Interface to high-performance periodic coupled-cluster theory calculations with atom-centered, localized basis functions

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Summary

A major part of computational materials science and computational chemistry concerns calculations of total energy differences and electronic excitations of poly-atomic systems. Currently, the most prevalent method for such computations is density-functional theory ([Hohenberg & Kohn, 1964](#)) (DFT) based on the Kohn-Sham formalism ([Kohn & Sham, 1965](#)) (KS) together with one of the numerous exchange-correlation (xc) approximations ([Civalleri et al., 2012](#); [Sousa et al., 2007](#)). The trade-off between comparably low computational cost and often reliably accurate results render it the dominant method in the field. Often, however, the accuracy of the xc approximations is not sufficient and uncertain, in particular when electronic correlations play a decisive role ([Savin & Johnson, 2014](#); [Zhang et al., 2016](#); [Zhang & Grüneis, 2019](#)).

Coupled-cluster (CC) methods ([Čížek, 1966](#)), while substantially more computationally expensive have proven to be significantly more accurate and reliable, at least for molecules and non-metallic solids. On these grounds, they allow for a systematic accuracy benchmark of other methods. Indeed, in molecular quantum chemistry the CC approach is considered the gold standard for a theoretical description of binding energies and electronic properties ([Chan, 2019](#)). It is typically used (at least) for benchmark studies. While the original CC methodology allows one to calculate the ground-state total energy of a system, it is also possible to compute properties of excited states using the equation-of-motion formalism of CC (EOM-CC) with comparable accuracy and reliability ([Stanton & Bartlett, 1993](#)). The conventional CC approach is limited, however, to systems with about 50 electrons ([Feller & Dixon, 2001](#); [Gyevi-Nagy et al., 2019](#)). By employing approximations, which exploit the locality of electronic correlation, materials with a couple of hundreds of electrons have been calculated via local natural orbital CC (LNO-CC) ([Nagy & Kállay, 2019](#)) and explicitly correlated pair natural orbital CC (PNO-CC-F12) ([Ma & Werner, 2021](#)). The extension of CC to periodic systems ([Hirata et al., 2004](#)) has been explored to a great degree by the research groups of [Andreas Grüneis](#) and [Garnet Chan](#).

In the work of [Andreas Grüneis et al.](#) the periodic formulation of CC was, for example, applied to study the adsorption behavior and surface chemistry of 2-dimensional materials including graphene ([Al-Hamdani et al., 2017](#)), boron nitride ([Brandenburg et al., 2019](#)) and surfaces ([Tsatsoulis et al., 2018](#)). These studies showed that CC yields consistently accurate adsorption energies and reaction energetics. The work of the groups of [Garnet Chan](#) and [Timothy Berkelbach](#) addressed the electronic properties of 2- and 3-dimensional materials. By applying the periodic equation-of-motion (EOM) CC formalism, band paths, optical spectra and band gaps of various materials (diamond, silicon, nickel oxide and others) have been investigated ([Gao et al., 2020](#); [McClain et al., 2017](#); [Wang & Berkelbach, 2020](#)).

It is important to note that all the periodic CC calculations published so far utilized pseudopotentials (Kresse & Joubert, 1999) to avoid explicit treatment of core electrons. One notable distinction between the works of the two groups is the type of basis set used. While the CC4S code of Andreas Grüneis et al. uses a plane-wave basis, the group of Garnet Chan performs their calculations using gaussian basis sets (McClain et al., 2017; Sun et al., 2018). Localized atom-centred basis sets like gaussian orbitals or numerical atomic orbitals (NAO) (Blum et al., 2009) can potentially decrease the computational cost. This is mostly due to the locality of the basis functions and their improved description of the atomic core region, which decreases the number of basis functions necessary for accurate computations of the system.

This paper describes a generalizable interface, called CC-aims, to the Coupled-Cluster for solids code (CC4S) developed by Andreas Grüneis et al. The interface is formulated in a general way and demonstrated here for the all-electron FHI-aims code (Blum et al., 2009). A generalization to other codes with atom-centered basis functions should be straightforward. This interface expands the power of electronic-structure theory codes to a variety of correlated methods. These include Møller-Plesset perturbation theory to second order (MP2), coupled-cluster theory including single and double excitations (CCSD) and CCSD including the perturbative treatment of triple excitations (CCSD(T)). Implementations of EOM-CC for neutral (EE-EOM-CC) and charged (IP-EOM-CC/EA-EOM-CC) excitations are currently under development. CC-aims can be used directly by any software package which uses a localized basis set and employs a resolution-of-identity scheme (Ren et al., 2012) (RI). This also includes local RI schemes, which expand products of atomic orbital basis function (AOs) pairs only using auxiliary basis functions that are localized on either of the atoms of the AOs. Primary examples for this family of localized schemes is the RI-LVL approach employed by FHI-aims (Ihrig et al., 2015), ADF (Förster & Visscher, 2020) and ABACUS (Lin et al., 2020) and the the pair-atomic RI (PARI) (Merlot et al., 2013). In addition to that, more conventional non-local schemes, which are predominantly used in molecular calculations, like RI-V (Whitten, 1973) and RI-SVS (Feyereisen et al., 1993) are recognized by CC-aims as well.

Statement of need

The CC-aims interface constitutes a practical alternative to each ab initio code implementing its own set of quantum chemistry wave function methods. Instead, CC4S and, by extension, CC-aims merely requires the ab initio code to provide a number of input quantities, most of which are generated during a Hartree-Fock or a Kohn-Sham calculation anyway. In return, the interfaced code gains access to an ever-growing number of wave function methods. The only input quantity of CC4S that is not typically calculated in quantum chemistry or electronic structure codes, but which is computed by CC-aims, is the Coulomb vertex (Hummel et al., 2017). The Coulomb vertex, a rank-3 tensor, constitutes a memory-saving approximation of the rank-4 tensor of Coulomb integrals. The storage of Coulomb integrals is the major memory bottleneck in CC calculations, so that the utilization of the Coulomb vertex expands the scope of system sizes which can be calculated. While in the case of localized orbitals the herein presented CC-aims interface can be used, in the case of plane-wave basis sets a different approach to calculate the Coulomb vertex has to be taken, which is described in (Hummel et al., 2017). For quantum chemistry programs employing a localized basis, an RI scheme is also needed (and thus may need to be implemented). CC-aims allows software packages which either lack certain quantum chemistry algorithms completely or which only offer insufficiently optimized implementations easy access to these methods. Interfaces like CC-aims will substantially accelerate the research done in areas where DFT is too inaccurate or too unreliable, by allowing many electronic structure codes to participate in these investigations without the time-consuming effort of implementing correlated wave-function methods.

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