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Coupled-Cluster Theory for Molecular Structure and Spectra: The Challenges Posed By Molecules and the Coupled-Cluster Solutions¹
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Coupled-cluster (CC) theory derives from the ansatz that the n-particle wavefunction is $|\Psi\rangle = \exp(T)|0\rangle$, where T is an excitation operator with $|0\rangle$ some choice of mean-field wavefunction. That is sufficient to obtain energies. But to obtain anything else, we use the CC functional, $E = \langle 0 | (1 + \Lambda) \exp(-T) H \exp(T) | 0 \rangle$, whose left and right hand eigenvectors provide energies and associated density matrices for the treatment of properties in CC theory. The introduction of Λ makes it possible to obtain the $\sim 3N$ forces associated with N atoms in the same time as the energy itself. This is essential information for indentifying the critical points on a potential energy surface and their associated Hessians, for either the prediction of vibrational spectra or to characterize a saddle point (transition state) for a reaction. A generalization of the functional to $\omega(k) = \langle 0 | L(k) \exp(-T) H \exp(T) R(k) | 0 \rangle$, provides excitation energies, $\omega(k)$ along with excited state left- and right-hand wavefunctions, Finally, with the response functions obtained from these left- and right-hand eigenfunctions, used in closed form, higher-order properties like NMR coupling constants are obtained. In this way, coupled-cluster theory provides a method that addresses all the properties of interest for molecules and their interactions. This development will be the topic of our contribution. For details please see, R. J. Bartlett and M Musial, "Coupled-cluster theory in quantum chemistry", *Revs. of Modern Phys.* **79**, 291-352 (2007).

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