DENSITY FUNCTIONALS FOR CORRELATION ENERGIES OF ATOMS AND MOLECULES

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I. INTRODUCTION

The correlation energy, $E_c$, is usually defined as the difference of the exact (non-relativistic) energy, $E$, and the Hartree-Fock (HF) energy, $E_{HF}$. $E_c$ is a very small part of $E$ only (1.4% for the He atom, 0.3% for Ne, 0.1% for Ar), but it is non-negligible in absolute value: for valence-shell removal, $\Delta E$ is 1.1 eV for He, 9.5 eV for Ne, and 9.3 eV for Ar. Inclusion of $E_c$ is important in cases where the number of (strongly interacting) electron pairs is changed, for dissociation energies ($D_e$), ionization potentials and excitation energies, e.g. Correlation is responsible for 23% of $D_e$ in the case of $H_2$, and for 84% of $D_e$ in the case of $Li_2$; $Na_2$ and $K_2$ are unbound at the HF level.

There is a number of methods for calculating $E_c$, among which are configuration interaction (CI), many-body perturbation theory (MBPT), and the density-functional (DF) method. Before concentrating on DF, a few remarks seem to be in order with regard to CI, the method which is most widely used in quantum chemistry nowadays. In the CI wave-function, excited configurations are admixed to the HF wave-function, $\phi_0$, and the expansion coefficients are determined by energy minimization. The expansion is usually restricted to single and double substitutions (CI-SD). CI-SD is not size-consistent ($E_c \sim \sqrt{N}$ for a system of $N$ non-interacting two-electron atoms), but unlinked-cluster effects can be introduced into CI-SD in a simple and efficient (although non-variational) way. Already with a few terms in the CI expansion, a substantial portion of the correlation contribution to dissociation energies can be obtained (70% for $F_2$, e.g., with two determinants, $\phi_0$ and $\phi(\sigma^2 \rightarrow \pi^2)$, if orbitals are optimized), but the convergence is extremely slow eventually;
Fig. 1. Correlation contributions to dissociation energies, \( \Delta D_e \) (au), for first-row monohydrides AH (N: number of electrons). +, * : exp. values from Refs. 8, 9.

a) \( E_c(AH) \approx E_c(A^+) + E_c(H^-) \); 
\( E_c(AH) \approx E_c(A^-) \).

b) \( E_c(A_{N-1}H) \approx E_c(A_N) \); CI results from Ref. 9.

up to \( 10^5 \) to \( 10^6 \) determinants are included in current CI calculations.

The convergence problem is intimately connected with the difficulty to describe the correlation cusp (cf. Sects. IV, VIIA) in a CI expansion. The accuracy of CI results for small molecules is impressive: for first- and second-row monohydrides, between 95\% (LiH) and 85\% (HCl) of the valence correlation energy is recovered; deviations from experiment are \( \pm 0.003 \) \( \text{\AA} \) for bond lengths \( r, \sim 14 \text{ cm}^{-1} \) for vibrational frequencies \( \omega_e, < 0.3 \text{ eV} \) for \( D_e \).

The DF method provides an economical and physically appealing alternative to CI calculations. The exact density functional is not explicitly known (perhaps very complicated), but simple local approximations exist (cf. Sects. III, IV). Are they expected to work? If so, simple relations should exist between correlation energies and densities; \( E_c \) should be similar, in particular, for atoms and molecules with similar densities. There are such relations, indeed, and we just call attention to three of them: i) total correlation energies of (neutral) atoms and molecules have been found to increase, to a good approximation, linearly with the number of electrons, \( E_c \approx -0.042 (N-1) \) au; \( \delta^6 \) actually, this is the most primitive form of a density functional for \( E_c \). ii) For first-row monohydrides, a good estimate of the correlation contribution to \( D_e \) is obtained from \( E_c(AH) \approx E_c(A^+) + E_c(H^-) \) at the beginning of the row, and from \( E_c(AH) \approx E_c(A^-) \) at the end of the row (cf. Fig. 1a). This can easily be rationalized in terms of the charge transfer in AH molecules which is \( A \rightarrow H \) at the beginning and \( H \rightarrow A \) at the end of the row. iii) The charge densities of the monohydrides should not be too different, on the other hand; from those of the united atoms; thus we expect \( E_c(A_{N-1}H) \approx E_c(A_N) \), where the index \( N \) refers to the electron number of the (neutral)