

## Artificial intelligence “sees” split electrons

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The glue that Nature uses to bind atoms together to make molecules and solids or liquids is the exchange-correlation (xc) energy, which expresses the lowering of the electrostatic repulsion energy between electrons due to their “social distancing”. Kohn-Sham density functional theory (1) tells us that the electron density determines this xc energy. This theory enables the efficient computer prediction of what molecules and materials can exist and with what properties, via the self-consistent solution of effective one-electron time-independent Schrödinger equations. However, the density functional or rule for Nature’s glue must be approximated. This is usually done by satisfying exact constraints or mathematical properties of the exact functional (which makes the approximation predictive), or by fitting to data (which makes it interpolative), or both. Two of the exact constraints, the ensemble-based piecewise linear variation of the total energy with respect to fractional electron number (2,3) and fractional electron  $z$ -component of spin (4), have remained very hard to satisfy by human ingenuity, although they are known to be important for the proper sharing of the electrons and their spins among the atoms. Their neglect leads to some of the worst qualitative failures of standard density functionals (5). Figure 1 illustrates this for a Na atom well separated from a Cl atom. The exact energy minimizes at zero electron transfer between neutral atoms, because the exact energy contribution from each atom is a linkage of straight line segments that connect with sharp corners at integer electron numbers, but simple density functionals that round off these corners minimize with non-zero electron transfer. A Cl atom that should have 17 electrons can wrongly have 17.4 electrons on average when its electron number fluctuates between 17 with 60% probability and 18 with 40% probability. While human beings learn the functional by positing equations, artificial intelligence (machine learning by deep neural networks) learns it by recognizing features and patterns in the data (6), somewhat in the same way that both human beings and

machines can recognize faces. This possibility was proposed by N.C. Handy at theoretical chemistry conferences in the 1990's. J. Kirkpatrick *et al.* (7) have taken a big step toward more accurate predictions for chemistry by the machine learning of molecular data plus the fractional charge and spin constraints, expressed as data that a machine can learn.

The resulting DeepMind 2021 (DM21) is technically a local hybrid functional, because it employs features or ingredients that can be constructed from the occupied Kohn-Sham one-electron wavefunctions, including the local spin densities, their gradients in space, the non-interacting kinetic energy, and the exact unscreened and screened exchange energy densities. DM21, which can be used with standard Kohn-Sham electronic structure codes, is fitted to some data sets for main-group molecules and then tested on others. On Grimme's very large and diverse suite of 55 data sets for different thermochemical energy properties (8), the weighted absolute error (WTMAD-2) of DM21 is 4.0 kcal/mol. This very small error is due to the large number of well-chosen ingredients and to the fitted molecular data. Table S6 of Ref. (7) shows that the error is essentially the same whether the fractional charge and spin data are included (DM21) or not (DM21m). But including those data improves the performance of DM21 for charge-transfer and strong-correlation problems not included in Grimme's test suite, such as binding energy curves for  $H_2^+$  and  $H_2$ , charge transfer in a DNA base pair, and a compressed hydrogen chain. DM21 impressively captures strong correlation without symmetry breaking.

For comparison, on the same suite of 55 test sets, the strongly constrained and appropriately normed (SCAN) functional (9) (without any exact exchange ingredient but with a standard dispersion correction) makes an 8.0 kcal/mol error (6). SCAN satisfies 17 exact constraints, but not the fractional charge and spin constraints, and is not fitted to any bonded system. When SCAN is density-corrected (evaluated on the Hartree-Fock density instead of its own self-consistent density), that error is reduced by about 2 kcal/mol (10). This density correction also eliminates charge-transfer errors of SCAN, but in an imperfect way.

For the chemistry of main-group elements, DM21 is remarkably good. As the authors explain, it may be less accurate for transition metal chemistry, a more challenging problem to which it is not fitted. Solids and liquids could also be described unsatisfactorily for several reasons: (1) They are not included in the DM21 fitting sets (although a variant of DM21 is fitted to the electron gas of uniform density). (2) Atoms and small molecules can be well described by using full exact

exchange at long range, while extended systems cannot. (3) The fractional spin constraint, while it is exact in principle, might suppress spin symmetry breaking (as it does for the binding energy curve of  $H_2$ ) that can be both real and revealing in extended systems.

In a 1972 *Science* essay, “More is Different” (11), P. W. Anderson explained that time-dependent fluctuations of the electron density or spin density persist over time scales that can grow large as the size of the system grows. These fluctuations break the symmetries that are found in an exact symmetry-preserving ground-state wavefunction, which may only predict the densities or spin densities averaged over an infinite time interval (12). For example, the net local spin density of an antiferromagnetic solid (e.g., *NiO*) can be zero over an infinite time interval, but can display localized spin moments that alternate in direction from one transition-metal atom to another in an ordered and fixed array, persisting for years. These local spin moments are predicted by standard spin density functionals, including SCAN. Supercell calculations (13) find that they (and the electrical insulation they produce) persist even above the antiferromagnetic ordering temperature. Because it can break symmetries, SCAN can both take account of and reveal the strong correlations that occur, for example, in the cuprate high-temperature superconducting materials, explaining both the insulator-to-metal transition that occurs with doping and the spin-and-charge stripes (14). Symmetry-breaking SCAN also works well for the hydrogen chain (13).

The importance of DM21 is not that it yields the ultimate density functional, but that, as its title suggests, it is “Pushing the frontiers of density functionals by solving the fractional electron problem”.

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Figure 1. Change in total energy of Na...Cl in the limit of infinite bond length, as a function of the change in electron number on the originally neutral Na atom due to electron transfer to the originally neutral Cl atom. A spurious electron transfer is predicted by the spin-unpolarized local density approximation (LDA) and by the spin-polarized local spin density (LSD) approximation, but not by the Perdew-Zunger self-interaction correction (SIC), which here imitates the straight-line segments of the exact Kohn-Sham density functional theory. (Figure adapted from Ref. (3).)

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