a different direction than before, albeit with the identical trigonal structure. The switching phenomena observed by Shen *et al.* might be peculiar for a material with a low crystallization temperature, fast crystallization speed, and large resistivity difference between the on and off states. At variance with a classic OTS, which is an electric field–driven switch, the tellurium switch gets its resistivity contrast from the metallic-like and semiconducting characteristics of its liquid and crystal phases, respectively.

The past half-century has seen major advances in communications and computing, and this trend is expected to continue at a high pace. Such expansion produces an exponential growth of big data, analyzed through artificial intelligence approaches on conventional computers. The demand for more computational power also comes with proportionally higher operational energetic costs. An increase in computational efficiency, offered by better devices, may be able to curb the carbon footprint that is generated, if the growth in efficiency can outpace demand. Looking at the potential breakthrough for applications, the integration of two single-element devices—that is, a single-element PC memory with a single-element switch—might be of interest. The single-element components will minimize element migration and enhance the robustness of the architecture. Shen *et al.* have proved tellurium to be the material of choice for the switch, whereas other researchers have suggested antimony as a promising candidate for a single-element PC memory (*9*). Furthermore, a scalability down to 60 nm has been demonstrated by the authors for a single XPoint element, with the on-current density increasing quadratically with decreasing device size while maintaining the same switching time, pointing at further scalability. What has been achieved by Shen *et al.* is unprecedented and provides a robust method to realize crystalline elemental switches that bear new perspectives for 3D XPoint architectures. ■

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QUANTUM CHEMISTRY

Artificial intelligence "sees" split electrons

Machine-learning creates a density functional that accounts for fractional charge and spin

By **John P. Perdew**

Chemical bonds between atoms are stabilized by the exchange-correlation (xc) energy, a quantum-mechanical effect in which "social distancing" by electrons lowers their electrostatic repulsion energy. Kohn-Sham density functional theory (DFT) (*1*) states that the electron density determines this xc energy, but the density functional must be approximated. This is usually done by satisfying exact constraints of the exact functional (making the approximation predictive), by fitting to data (making it interpolative), or both. Two exact constraints—the ensemble-based piecewise linear variation of the total energy with respect to fractional electron number (*2*) and fractional electron z-component of spin (*3*)—require hard-to-control nonlocality. On page 1385 of this issue, Kirkpatrick *et al.* (*4*) have taken a big step toward more accurate predictions for chemistry through the machine learning of molecular data plus the fractional charge and spin constraints, expressed as data that a machine can learn.

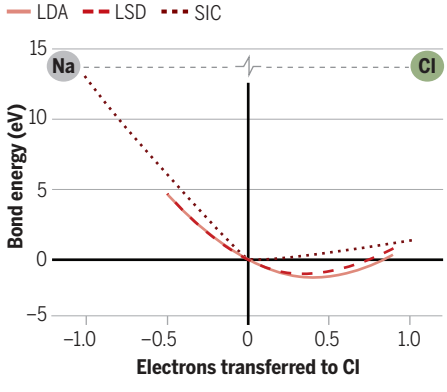
Efficient computer prediction of what molecules and materials can exist, and with what properties, can be enabled with DFT, through the self-consistent solution of effective one-electron time-independent Schrödinger equations. However, in cases in which exact constraints are important for the proper sharing of the electrons and their spins among the atoms, their neglect can lead to some of the worst qualitative failures of standard density functionals (*5*). This problem can be illustrated by the case of a sodium (Na) atom well separated from a chlorine (Cl) atom (see the figure) (*6*). 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. However, simple density functionals that round off these corners minimize with nonzero electron transfer. A Cl atom that should have 17 electrons might wrongly be assigned on average 17.4 electrons because its electron number fluctuates between 17 with 60% probability and 18 with 40% probability.

Human beings have developed approximations to the exact density functional by positing equations and determining how well they agree with exact solutions and experimental data. Artificial intelligence (machine learning with the use of deep neural networks) could learn it by recognizing features and patterns in the density after training on similar data (*7*). This process is analogous to the way that both human beings and machines can recognize faces.

The DeepMind 2021 (DM21) functional developed by Kirkpatrick *et al.* is technically a local hybrid (nonlocal) functional. It has features that can be constructed from ingredients such as the local spin densities, their gradients in space, the noninteracting kinetic energy densities, and the exact unscreened and screened exchange energy densities. DM21, which can be used with standard Kohn-Sham electronic structure

Not staying neutral

In the limit of an infinite bond length, sodium chloride (NaCl) should be neutral atoms, not ions. The total energy should follow the straight-line segments of the exact Kohn-Sham density functional theory, as imitated by the Perdew-Zunger self-interaction correction (SIC) functional. However, a spurious transfer of 0.4 electrons to Cl is predicted by the spin-unpolarized local density approximation (LDA) and by the spin-polarized local spin density (LSD) approximations.



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codes, was fit to some data sets for main-group molecules and then tested on others. On a large and diverse suite of 55 data sets for different thermochemical molecular properties (*8*), the weighted absolute error of DM21 is 4 kcal/mol.

This very small error compared with that for most functionals results from the large number of well-chosen ingredients and from the fitted molecular data. The error is essentially the same whether the fractional charge and spin data are included (DM21) or not (DM21m). However, inclusion of those data improved the performance of DM21 for charge-transfer and strong-correlation problems not included in the 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.

A comparison can be made to the strongly constrained and appropriately normed (SCAN) functional (*9*), which was created by positing equations that satisfy 17 exact constraints but not the fractional charge and spin constraints. Unlike DM21, SCAN is not fitted to any bonded system and does not use expensive exact exchange. On the same suite of 55 test sets, without any exact exchange ingredient but with a standard dispersion correction, SCAN makes an 8 kcal/mol error. However, when SCAN is density-corrected (evaluated on the Hartree-Fock density instead of its own self-consistent density), that error is reduced to 6 kcal/mol (*10*). This density correction also eliminates charge-transfer errors of SCAN.

For the chemistry of main-group elements, DM21 is very good, although it may be less accurate for transition metal chemistry, a more challenging problem to which it was not fitted. Solids and liquids could also be described unsatisfactorily for several reasons: because they are not included in the DM21 fitting sets (although a variant of DM21 was also fit to the electron gas of uniform density) and because atoms and small molecules can be well described by using full exact exchange at long range, whereas extended systems cannot.

The fractional spin constraint in DM21, although 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. As noted by Anderson (*11*), 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 to that of a crystal lattice. These fluctuations break the symmetries that are found in an exact symmetry-preserving ground-state wave function, 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 such as nickel oxide (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 and persist for years.

These local spin moments can be predicted by use of standard spin density functionals, including SCAN. Supercell calculations (with larger than minimal unit cells) (*13*) find that those moments (and the electrical insulation they produce) persist even above the antiferromagnetic ordering temperature. Because it can break symmetries, SCAN accounts for and reveals 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 developed by Kirkpatrick *et al.* is not that it yields the ultimate density functional but that an artificial intelligence (AI) approach addressed the fractional electron and spin problem that has resisted a direct analytical solution to creating the functional. Their work and that of (*15*) suggest that more predictively accurate density functionals can be designed by combining constraint satisfaction with AI fitting to large and diverse data sets. ■

GRAPHIC: ADAPTED FROM (6) BY K. FRANKLIN/*SCIENCE*

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PLANETARY SCIENCE

Martian water escape and internal waves

Lower atmospheric processes are vital for assessing water loss from Mars

By **Erdal Yiğit**[1,2]

Evidence has accumulated in recent years that suggests that Mars used to have more habitable conditions (*1*). Determining the processes that led to its current cold and dry state are important for understanding habitability more generally. Observations and modeling efforts show that atmospheric escape has adversely affected Mars' habitability primarily by irreversibly diminishing the atmospheric water reservoir through loss of atomic oxygen and hydrogen into space (*2*). Understanding this requires connecting dust storms, atmospheric waves, and atmospheric water.

Geological considerations require that water was more abundant on Mars early in its history, along with Mars being wetter and warmer (*1*). The thermal escape of atomic hydrogen (H) to space is the primary mechanism for long-term loss of water (see the figure). Molecular hydrogen (H_2) forms in the middle atmosphere by photochemical processes (*3*) and is transported upward, where it is decomposed to H, which can more easily escape to space (*4*). Recent general circulation modeling studies (*5*), as well as observations by the MAVEN (Mars Atmosphere and Volatile Evolution) spacecraft (*6*) and the ExoMars Trace Gas Orbiter (TGO) (*7*), demonstrated that water can be directly transported during the perihelion season to the thermosphere, where it is dissociated. However, the role of the lower atmospheric weather and the associated wave-induced vertical coupling processes are insufficiently explored.

Processes that led to the loss of water on Mars are complex and require a whole-

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Science

Artificial intelligence “sees” split electrons

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