An interpretive dance in three movements

Peter M.W. Gill, Laura K. McKemmish, Yves A. Bernard, Pierre-François Loos

Research School of Chemistry, Australian National University, Australia

Science Road, Canberra ACT 0200, Australia. peter.gill@anu.edu.au

Amazing advances in computer hardware and quantum chemistry software have allowed researchers to generate large volumes of numbers in small amounts of time. However, this is a dangerous situation. Speakers in the "Interpretation Models" session will respond to Coulson's famous plea: "Give me insight, not numbers!"

My lecture will consist of three movements:

In the first movement, I will describe work with my student Laura McKemmish, whose PhD research has helped to explain why quantum chemical calculations in which the molecular orbitals are expanded in a Gaussian basis set, *e.g.*

$$\exp(-r) \approx \sum_{i=1}^{n} c_i \exp(-\alpha_i r^2) \tag{1}$$

exhibit surprising convergence behaviour [1].

In the second movement, I will describe work with my student Yves Bernard, whose PhD research showed that, although the Heisenberg Uncertainty Principle does not allow us to follow the path of an electron in a molecule, we can nonetheless use the posmom variable [2]

$$s = \mathbf{r} \cdot \mathbf{p} \tag{2}$$

and its quantum mechanical density $S(s)$ to learn something about the trajectories of such particles.

In the final movement, I will describe work with my colleague Pierre-François Loos, whose research on electrons moving on rings [3] shows why the Local Density Approximation (LDA)

$$E_c^{\mathrm{LDA}}[\rho] \approx \int F(\rho(\mathbf{r}))\rho(\mathbf{r})\,d\mathbf{r} \tag{3}$$

seriously overestimates molecular correlation energies and has indicated how an improved version of the LDA can be systematically constructed.

[1] McKemmish, L.K. and Gill, P.M.W. *J. Chem. Theory Comput.*, 8:4891-4898, 2012.

[2] Bernard, Y.A. and Gill, P.M.W. *New J. Phys.*, 11:083015/1-15, 2009.

[3] Loos, P.F. and Gill, P.M.W. *J. Chem. Phys.*, 138:164124/1-9, 2013.