Effective Potentials: Collaborative Studies with James D. Talman

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Szabo and Ostlund[1] wrote, "At first glance it does not appear possible to construct an *exact* one-particle theory since the many-electron Hamiltonian contains two-particle interactions. F. Dyson surmounted this apparent difficulty by introducing an effective potential which was *energy dependent*, called the *self-energy*. Moreover, he showed that the exact $\boldsymbol{G}(E)$ obeys the integral equation [...]:" This is the foundation of one-particle many-body Green's-function theory.

Density-functional theory (DFT) is another formally *exact* one-particle theory. It too employs an effective potential called the exchange-correlation potential. In the exchange-only approximation, the corresponding potential, thus *exact-exchange DFT*, has been identified as the optimized effective potential (OEP) of Talman and Shadwick.[2] It is obtained by solving the OEP integral equation and can be energy dependent.[3] The Hartree–Fock (i.e., exchange) self-energy and OEP are related to each other by the Sham–Schlüter equation.[4] It is the foundation of *ab initio* DFT of Bartlett's.

Here, I present studies conducted in direct collaboration with or inspired by Dr. James D. Talman, a polymath from whom I have had the privilege of learning over the 15 years of friendship. They include (1) a Gaussian-basis-set algorithm of the OEP integral equation and the question about the uniqueness of its solution; (2) an extension of OEP to the correlation potential; (3) an extension to excited states via the time-dependent DFT formalism without or with an energy-dependent exchange kernel; (4) a grid-based solution of the Hartree–Fock equation; (5) a grid-based solution of the Sinanoğlu equation and effective correlation potentials; (6) general-order many-body Green's function theory and self-energies. They share the common goal of achieving systematically accurate yet compact *effective potentials* an electron feels in the sea of the other electrons in atoms, molecules, and solids.

[1]A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry*, Macmillan, New York, 1982.
[2]J. D. Talman and W. F. Shadwick, *Phys. Rev. A* **14**, 36 (1976).
[3]A. Görling, *Phys. Rev. A* **57**, 3433 (1998).
[4]L. J. Sham and M. Schlüter, *Phys. Rev. Lett.* **51**, 1888 (1983).