What’s next?

Considering the chapters of this book as a road-map for the progress in the field of many-electron theories along the path of multi-disciplinarity, one can draw some basic conclusions. It is clear that computational physics and chemistry are going to have a role of increasing importance in the description of many-electron systems, as technological progress leads to ever more powerful computers. It is also clear that the other disciplines can certainly help this process assuring the highest efficiency in developing computational algorithms. However, beyond applications, the investigation of fundamental questions of many-electron systems is by far not saturated. This implies that while on one side we will have increasingly efficient and accurate numerical descriptions of matter, with system sizes and time scales directly comparable to those of experiments, on the other side, part of our effort should be devoted to the analysis of fundamental aspects of the problem which up to now did not find a satisfactory treatment. Mel Levy and Elliott Lieb are two of the most prominent researchers who have dedicated their efforts to the investigation of fundamental questions in many-electron theory. Their results have not only revolutionized the theoretical approach of the field, but, directly or indirectly, allowed for a quantum jump in the computational treatment of realistic systems as well. For this reason, at the conclusion of this journey across different disciplines, we have asked Mel Levy and Elliott Lieb to provide us with a list of open problems, summarized below, which they believe...
Two open problems formulated by Mel Levy

- **Is there a closed form expression for ground-state energy from ground-state density?**

For the interacting physical system of interest, assume that one is given the exact ground-state density, \( \rho(\mathbf{r}) \), associated with electron-nuclear attraction potential \( v(\mathbf{r}) \). Is there a closed-form expression that gives the ground-state energy, \( E_{gs} \), in terms of \( \rho(\mathbf{r}) \) and \( v(\mathbf{r}) \)?

I am not aware of a theorem that states that the answer is definitely no because the system is interacting. In fact the answer would be yes if each term in the electron-electron repulsion operator were squared. Then, for instance, \( E_{gs} \) would equal \((1/2)V_{en}\) for an atom, where \( V_{en} \) is the electron-nuclear attraction energy. This result follows from use of the virial theorem with the fact that the electron-electron repulsion operator here exhibits the same homogeneous coordinate scaling as the kinetic operator. Perhaps the answer is also yes for real physical systems, with a more complicated relation.

Presently, there are known bounds for real physical systems with exact electron-electron repulsion operators. For instance, it can be shown that:

\[
(1/2)V_{en} < E_{gs} < (1/3)V_{en} \tag{1}
\]

for any atom, and there exist analogous bounds for any system. For systems other than atoms, gradients of \( v(\mathbf{r}) \) or \( \rho(\mathbf{r}) \) are needed. The left inequality simply comes from using the virial theorem and neglecting half the electron-electron repulsion. The right inequality comes from use of a generalized variational theorem where the number of electrons in the wave function is greater than in the Hamiltonian.

- **Is the Ionization Energy always greater than the Electron Affinity for Coulomb systems?**

To my knowledge there is no proof that the ionization energy is always greater than the electron affinity for Coulomb systems, even though this property is so very important in the study of band gaps and strong correlations. In other words, there does not appear to be a general proof that \( I[N+1] < I[N] \) where \( I[M] \) is the ionization energy of the M-electron system. It should be noted, however, that the special case \( I[2] < I[1] \) has
been shown [10]. Also, exceptions to $I[N + 1] < I[N]$ have been found for non-Coulomb systems[6]. The property $I[N + 1] < I[N]$ can be proven for certain Coulomb atoms. Consider those atoms for which $I[N + 1] < I[N]$ when the electron-electron repulsion is absent. For these atoms, it can be shown that $I[N + 1] < I[N]$ when the full electron-electron repulsion operator, $V_{ee}$, is present, provided that the nuclear charge is high enough. This result follows from use of coordinate scaling.

An Open Problem about exchange-correlation energy formulated by Elliott Lieb

The Lieb-Oxford Inequality [7] states that, for any normalized, symmetric or anti-symmetric $N$-particle wave function, $\Psi_N$,

$$\left\langle \Psi_N \right| \sum_{1 \leq m < n \leq N} \frac{1}{|x_m - x_n|} \Psi_N \right\rangle \geq \frac{1}{2} \int \rho_\Psi(x) \rho_\Psi(y) \, d^3x \, d^3y \right\rangle - C_{LO} \int \rho^{4/3}_\Psi(x) \, d^3x,$$

where $C_{LO} = 1.68$ and

$$\rho_\Psi(x) = N \int |\Psi(x, x_2, \ldots, x_N)|^2 \, d^3x_2 \cdots d^3x_N$$

is the one-particle density corresponding to $\Psi_N$, with $\int \rho_\Psi(x) \, d^3x = N$. The first term on the right side is called the direct energy and the difference between it and the left side of (2) is called the exchange-correlation energy and is denoted by $E_{xc}$. Thus, (2) gives a lower bound to $E_{xc}$ and the goal is to improve it. Motivated by inequality (2), much effort [1, 2, 4, 8, 9, 11] has gone into determining the optimal value for the constant, which lies between about 1.45 and 1.68. The number 1.45 is based on numerical values for the charged electron gas in a uniform background. A rigorous lower value of 1.23 for $C_{LO}$ was obtained in [7]. Current opinion is that the true answer is close to this 1.45 figure.

The inequality (2) is also valid for a density matrix that is not a pure state, but we will continue to think in terms of $\Psi$.

On the other hand, Dirac had shown much earlier [5] that for a free Fermi gas in its lowest energy state, the above inequality would become an asymptotic equality, for large $N \gg 1$ by replacing $C_{LO}$ by the spin-dependent constant $C_D = 0.93q^{-2/3}$, where $q$ is the number of spin states available to the fermions. Electrons have $q = 2$ and in this case $C_D = 0.93 \cdot 2^{-1/3} = 0.74 \ll 1.68$. 

On Some Open Problems in Many-Electron Theory

3
The open problem discussed here is how to reconcile the Dirac $E_{xc}$ and the $-C_{LO}\int \rho_{\Psi}^{4/3}$ lower bound for $E_{xc}$ in (2). Before presenting it in detail, let us first mention a problem that looks similar, but is quite different.

There are quite a few papers in the literature that try to take into account the variation of $\rho_{\Psi}(x)$ with $x$. An especially interesting result is by Benguria, Bley and Loss [3] who (essentially) bound $E_{xc}$ by $-1.45 \int \rho_{\Psi}^{4/3} - C' (\rho_{\Psi}^{1/2} ||p|| \rho_{\Psi}^{1/2})$ for some constant $C'$ and where $|p| = \sqrt{\nabla^2}$. They note that the added term, $-C'(\cdots)$ is often very small compared to the first term and, therefore, the effective constant is approximately $1.45$, as anticipated.

Our open problem is, however, not about the effect on $E_{xc}$ of the spatial variation of the quantity $\rho_{\Psi}(x)$, which is, after all, the envelope of the many-body wave function. It refers to the internal local kinetic energy, which is present even where $\rho_{\Psi}$ is constant and which is not visible in $\rho_{\Psi}$. The LO bound on $E_{xc}$, whatever the sharp constant $C_{LO}$ might turn out to be, is relevant only if the underlying wave function has a kinetic energy that is much higher than the minimum kinetic energy density for a gas having particle density $\rho$, which equals

$$\frac{3}{2}(6\pi^2)^{2/3} q^{-2/3} \rho_{\Psi}(x)^{5/3}.$$ 

If the kinetic energy is close to this minimum then the Dirac constant 0.74 is relevant. If it is far from this minimum then the constant $C_{LO}$ is relevant.

We may define the kinetic energy density as the positive function

$$T_{\Psi}(x) = N \int |\nabla_{x_2} \Psi(x_1, \ldots, x_N)|^2 dx_2 \cdots dx_N, \quad (4)$$

Clearly, the total kinetic energy is $T = \int T_{\Psi}(x) d^3x$, just as the particle number is $N = \int \rho_{\Psi}(x) d^3x$. Since quantum mechanics can be formulated in momentum-space as well as in $x$-space, $T_{\Psi}(x)$ should be as relevant as $\rho_{\Psi}(x)$.

**OPEN PROBLEM**: Find a lower bound to $E_{xc}$ that involves both $T_{\Psi}(x)$ and $\rho_{\Psi}(x)$ by using the ratio

$$R_{\Psi}(x) = \frac{T_{\Psi}(x)}{\frac{3}{2}(6\pi^2)^{2/3} q^{-2/3} \rho_{\Psi}(x)^{5/3}}$$

to improve the LO type bound (or some other bound) in a way that (locally) reduces to the Dirac $E_{xc}$ when $R_{\Psi}(x)$ is small. When $R_{\Psi}(x)$ is large the effective constant (locally) should be $C_{LO}$.

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