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A one-to-one mapping between the one-particle densities and a particular set of n-particle ensembles is constructed. The construction entails simultaneous minimization of the energy and minimization of the L_2-norm over the set of ensembles which yield a given density. Differences between the present approach to density functional theory and other approaches, such as Kohn-Sham theory (Ref. 12) and Thomas–Fermi–Dirac–Weizsacker theory (Ref. 13) are emphasized. The Levy density functional may be decomposed into kinetic and electron-electron interaction components.

I. THE HOHENBERG–KOHN THEOREM

The central problem of density functional theory is to define the energy of an arbitrary one-electron density. For a certain set of these densities, Hohenberg and Kohn[1] (HK) were able to demonstrate the existence of an energy-density functional which obeys the variational bound, E_0, of the original Schrödinger functional,[2]

$$E_s[\Psi] \equiv \langle \Psi, H\Psi \rangle \geq E_0 . \tag{1}$$

Here, Ψ is some unit-normalized, antisymmetric wave function and H is a fixed, molecular Hamiltonian. For certain densities, the HK theorem assigns an energy such that

$$E_{HK}[\rho] \geq E_0 . \tag{2}$$

A characterization of these densities follows.

A density ρ is said to be representable by a wave function Ψ if

$$\rho(x) = \int dx_{N-1} \Psi(x, x_{N-1}) \Psi^*(x, x_{N-1}) , \tag{3}$$

where $x_K = (x_1, \ldots, x_k)$ is a vector of spin-space coordinates. If ρ is representable by a nondegenerate, normalized, antisymmetric wave function that is also the ground state for a system with some local, external potential, $v(r)$,[3] ρ is said to be v representable. These are the densities for which the HK theorem assigns an energy.

The key to the construction of $E_{HK}[\rho]$ is that there is only one such wave function for each density.[1] Now it is easy to assign an energy to ρ:

$$E_{HK}[\rho] \equiv \langle \Psi(\rho), H\Psi(\rho) \rangle , \tag{4}$$

where $\Psi(\rho)$ is the parametrization of the set of nondegenerate, ground-state wave functions generated by the distinct density each produces. Further, this parametrization is independent of the local, external potential in H. Consequently, one says that $E_{HK}[\rho]$ is universal as a functional of ρ. Note that Eq. (4) only calls for the computation of expectation values which already appear in the usual Schrödinger functional. Therefore, the variational bound, Eq. (2), holds for all v-representable

ρ. If $H\Psi_0 = E_0\Psi_0$, and $\int dx_{N-1} \Psi_0\Psi_0^* = \rho_0$, then $E_{HK}[\rho_0] = E_0$.

There is both an advantage and a disadvantage to the HK formulation of density functional theory. The advantage is that there is a one-to-one mapping between at least some densities and some wave functions that allows E_{HK} to be decomposed into kinetic and interaction parts. The disadvantage is that it not known whether or not $E_{HK}[\rho]$ is defined for all ρ.

Fortunately, Levy[4] has proposed an alternative definition of the energy of an density which is valid for any density, making use of the fact that Gilbert[3] has shown that any density may be derived from at least one wave function. However, in this approach the one-to-one mapping between densities and wave functions is lost, along with the decomposition. Recovery of such a mapping will require a slight modification of Levy's approach.

II. THE LEVY FUNCTIONAL WITH MODIFICATIONS

Recently, Levy[4] proposed a different concept of the energy of a density, defined for an arbitrary density. However, in his scheme, generally many wave functions give the same density and have that energy which one wants to assign to that density. The relationship between densities and wave functions in Levy's theory is no longer one-to-one.

The following modification of the Levy functional will be helpful in recovering a one-to-one mapping. It was suggested previously[5] that one regard one-particle densities as originating from ensembles or n-particle density matrices (or n matrices), rather than from simple wave functions. An n matrix, $D(N, N')$, may be defined as

$$D(N, N') = \sum_k w_k \Psi_k(N)\Psi_k^*(N') , \tag{5}$$

where N is the set of spin-space coordinates, $(x_1, \ldots, x_n)$, $\{\Psi_k\}$ is some set of orthonormal, antisymmetric n-particle functions, and $\sum_k w_k = 1$, with all $w_k \geq 0$. The set of all such n matrices we denote as $\mathscr{E}_n$. The one-particle density may now be generated by the integral

$$\rho_D(x) = \int dx_{N-1} D(x, x_{N-1}; x, x_{N-1}) . \tag{6}$$

We label the set of all n matrices that produce the same density $L_\rho(n) \subset \mathscr{E}_n$:[6]

$$L_\rho(n) \equiv \left\{ D \in \mathscr{E}_n : \int dx_{N-1} D(x, x_{N-1}; x, x_{N-1}) = \rho(x) \right\} , \tag{7}$$

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for one fixed ρ. None of the $L_\rho(n)$ are empty as stated previously.[3] Then the energy-density functional $E_e[\rho]$[4,5] may be defined as

$$E_e[\rho] \equiv \min\{\langle H, D\rangle : D \in L_\rho(n)\} . \qquad (8)$$

The inner product notation, $\langle A, B\rangle$, for matrices A and B, is adopted.[6] Thus the energy for an arbitrary density is the least energy of all ensembles in $L_\rho(n)$. In general, there are many ensembles that produce the same energy. Our goal is to define a selection process that chooses a unique ensemble from those in $L_\rho(n)$ with least energy.

III. A ONE-TO-ONE MAP BETWEEN THE SET OF DENSITIES AND A SET OF ENSEMBLES

Let $L_\rho(n, E_e) \subset L_\rho(n)$ be the set of ensembles in $L_\rho(n)$ that also have least energy. The set $L_\rho(n, E_e)$ is convex[7] and is part of a Hilbert space.[6] The inner product on this Hilbert space is

$$\langle D, D\rangle = \mathrm{tr} D^2 . \qquad (9)$$

This inner product induces a norm on the Hilbert space given by

$$\|D\| \equiv \langle D, D\rangle^{1/2} . \qquad (10)$$

Now take the minimum of this norm over $L_\rho(n, E_e)$:

$$\delta = \min\{\|D\| : D \in L_\rho(n, E_e)\} . \qquad (11)$$

Because $L_\rho(n, E_e)$ is convex, there is only one ensemble that attains this minimum, δ.[8] This is the unique ensemble which we associate with the density: $D(\rho)$ simultaneously minimizes the energy and the norm on the ensembles over $L_\rho(n)$.

For concreteness we suppose that $L_\rho(n, E_e)$ is part of a finite-dimensional space. We assume that $L_\rho(n, E_e)$ can be spanned by a finite number of its orthonormal elements, $\{D_i\}_{i=1,\ldots,s}$. So, for any $D \in L_\rho(n, E_e)$,

$$D = \sum_{i=1}^{s} a_i D_i , \qquad (12)$$

where $\sum_{i=1}^{s} a_i = 1$ and $a_i \geq 0$. Then, the minimum-norm element $D_{\min}$ is the one with all $a_i = 1/s$:

$$D_{\min} = \frac{1}{s} \sum_{i=1}^{s} D_i . \qquad (13)$$

This is the equal-occupancy ensemble, which seems reasonable, physically, since there is no a priori reason for choosing any one of these representations over the others.

We now identify $E_e[\rho]$ as

$$E_e[\rho] \equiv \langle H, D(\rho)\rangle = \langle H(N), D(N, N'; \rho)\rangle , \qquad (14)$$

where $D(\rho)$ now plays the role of $\Psi(\rho)$ in Eq. (4). It signifies the parametrization of the critical set of ensembles which we previously described by the unique densities that they produce. This situation is essentially the one present in the original HK theorem, except that Eq. (14) is defined for all densities.

$$\langle H, D\rangle = n \int d\vec{x}\, v(x)\rho(x) + \langle T + V_{ee}, D\rangle , \qquad (15)$$

for all $D \in L_\rho(n)$, where T and V_{ee} are the n-particle kinetic and electron–electron interaction energies, $D(\rho)$ must be independent of the local, external potential, v. Therefore, we consider $E_e[\rho]$ to be a universal functional of the density.

Two remarks are in order at this point. First, there is no reason to believe that the foregoing is the only conceivable selection process. This may have an influence on the properties of $D(\rho)$. Second, a similar theory for reduced matrices exists, and in particular for one-matrices denoted by γ,[6] with results similar to those of this paper. The difference is that the mapping between reduced matrices and n-matrices is slightly different. In particular, there are more one-matrices than densities. Consequently, $D(\gamma)$ is "more detailed" than $D(\rho)$. The importance of this is that $D(\gamma)$ might contain more critical points of the original Schrödinger theory, thereby increasing the possibility that $D(\gamma)$ might include excited-state ensembles, while $D(\rho)$ might not.

IV. DISCUSSION AND EXTENUATING PROBLEMS

Since a single-valued function $D(\rho)$ now has been constructed, the situation now seems more amenable to the exploration of advanced topics centered about differentiability and the presence of excited states. Should the functional $E_e[\rho]$ of Eq. (14) prove to be continuously differentiable, Euler equations for this functional would actually exist.[9] An explicit Euler equation would facilitate the answering of the question of the presence of excited states in this approach to density functional theory.

First considering differentiability, it should be noted that $E_e[\gamma]$ might be differentiable, while $E_e[\rho]$ might not. A full analysis is not yet available. However, possible differences between the two functionals are indicated in the analysis of continuity. In the case of $E_e[\gamma]$, we have the following results from Kato[10] and Klahn and Bingel[11]:

$$\langle V_{ee}, D\rangle \leq K + \langle T, D\rangle . \qquad (16)$$

The constant K is independent of D, but

$$\langle T, D\rangle = \langle t, \gamma\rangle , \qquad (17)$$

where t is the reduced, one-particle kinetic energy operator. Thus, all ensembles yielding a particular γ have energies bounded above by a constant related to $K + \langle t, \gamma\rangle$. This is enough to show that $E_e[\gamma]$ is continuous with respect to changes in γ, in the norm given in Refs. 10 and 11.

In the case of $E_e[\rho]$, relations similar to Eq. 16 are not known. So continuity is not as easily established in this instance. Being concerned with minimum-energy ensembles in $L_\rho(n)$, which cannot become too negative by the variational principle, there is a good deal of hope in this case, nevertheless.

One may consider a related question. Suppose ρ_j and γ_j correspond to an excited-state wave function Ψ_j. It might be true that

$$D(\gamma_j) = \Psi_j \Psi_j^* \qquad (18)$$

and

$$D(\rho_j) = \tfrac{1}{2}\left[\Psi_j(N)\Psi_j^*(N') + \Psi_j^*(N)\Psi_j^*(N')\right] . \qquad (19)$$

That is, $\Psi_j\Psi_j^*$ or $\tfrac{1}{2}[\Psi_j(N)\Psi_j^*(N') + \Psi_j^*(N)\Psi_j(N')]$ might be an energy-minimizing ensemble in either $L_{\gamma_j}(n)$ or $L_{\rho_j}(n)$, respectively. Note that it may be possible for Eq. (18) to be true without Eq. (19) being true. It is first necessary to verify (or disprove) this conjecture, if one wishes to deal with excited states in this theory. It is expected that Harriman's work[6] will be of importance in this connection. Assuming the conjecture to be true, one must then determine whether or not $E_e[\rho_j]$ or $E_e[\gamma_j]$ is an extremum.[9]

Another concern in this work is the development of an adequate framework for the systematic approximation of $E_e[\rho]$. It is hoped that this has been accomplished through the introduction of the well-characterized sets, $L_\rho(n)$, and the establishment of the single-valued function $D(\rho)$, defined for all ρ. It should be clear that the present point of view is very different from the Kohn–Sham theory[12] and the Thomas–Fermi–Dirac–Weizsacker theory.[13] This is due to the decision to adhere rigorously to the variational principle. It appears that other theories develop their functionals with different considerations in mind. In particular, I do not believe that any existing, approximate density functional theory has been constructed with the prescriptions of Eq. (14) enforced.[14] Therefore, an approximation based on the properties of $E_e[\rho]$ promises to provide novel information.

Of course, the nature of the parametrization, $D(\rho)$, is not completely understood. For instance, is it possible to apply a ρ-dependent transformation to $D(\rho)$ which will bring it to diagonal form as in Eq. (5)? Two other properties of $D(\rho)$ are evident though. One is that the parametrization does not require the knowledge of the derivatives of the density. The other is that Eq. (14) is valid for any density, whether or not it is given in terms of an orbital decomposition. Similar remarks are also true for $E_e[\gamma]$. As pointed out in Ref. 5, the analysis of Donnelly and Parr[15] holds for $E_e[\gamma]$. From the remarks above, the total variation of $E_e[\gamma]$ with respect to γ, as contemplated in Ref. 15, is a reasonable notion to entertain. However, because of the parametric nature of $D(\gamma)$, Eqs. (20) and (22) of Ref. 15 still seem unreasonable, as previously suggested.[5] As demonstrated by Harriman,[6] the introduction of an orbital basis greatly increases the degree of clarity in the structure of $L_\rho(n)$ and its one-matrix analogs.

V. SUMMARY

A parametrization, $D(\rho)$, of a set of ensembles as a function of the one-electron density has been constructed, using a modification of the Levy functional and the Hilbert space structure of the set of ensembles. This parametrization permits an energy and unique ensemble to be assigned to any density. The parametrization enhances the prospects for obtaining Euler equations for the derived functional, $E_e[\rho] = \langle H, D(\rho) \rangle$. Separation of this functional into kinetic and potential parts permits different approximations for each.

ACKNOWLEDGMENT

[1] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).

[2] I. N. Levine, *Quantum Chemistry* (Allyn and Bacon, Boston, 1974), Chapter 8. Also, see most other introductory quantum mechanics texts.

[3] T. L. Gilbert, Phys. Rev. B **12**, 2111 (1975).

[4] M. Levy, Proc. Natl. Acad. Sci. USA **76**, 6062 (1979).

[5] S. M. Valone, J. Chem. Phys. **80**, 1344 (1980).

[6] J. E. Harriman, Phys. Rev. A **17**, 1249, 1257 (1978).

[7] If $a_1, \ldots, a_m$ is a set of vectors, then a convex combination of the a_i is a sum of the a_i with all coefficients between 0 and 1 and the sum of the coefficients themselves is 1:

$$a = \sum_{k=1}^{m} w_k a_k \, ,$$

with $w_k \geq 0$ for all k and $\sum_{k=1}^{m} w_k = 1$. See also R. M. Erdahl, Int. J. Quant. Chem. **13**, 697 (1978).

[8] E. Kreyzig, *Introductory Functional Analysis with Applications* (Wiley, New York, 1978), pp. 142–145 and Theorem 3.3-1, in particular.

[9] I. M. Gelfand and S. V. Fomin, *Calculus of Variations*, revised English ed., translated by R. A. Silverman (Prentice-Hall, Englewood Cliffs, New Jersey, 1963), pp. 8–14.

[10] T. Kato, Trans. Am. Math. Soc. **70**, 195 (1951).

[11] B. Klahn and W. A. Bingel, Theor. Chim. Acta **44**, 9 (1977).

[12] W. Kohn and L. S. Sham, Phys. Rev. **140**, A1133 (1965); A. Zunger and M. L. Cohen, Phys. Rev. B **18**, 5449 (1978); **20**, 4082 (1978).

[13] D. A. Kirzhnits, Zh. Teor. Fiz. **32**, 115 (1957); [Sov. Phys. JETP **5**, 64 (1957)]; C. H. Hodges, Can. J. Phys. **51**, 1428 (1973); W.-P. Wang, R. G. Parr, D. R. Murphy, and G. A. Henderson, Chem. Phys. Lett. **43**, 409 (1976).

[14] E. H. Lieb, Phys. Lett. **70A**, 444 (1979); J. D. Doll and W. D. Reinhardt, J. Chem. Phys. **57**, 1169 (1972).

[15] R. A. Donnelly and R. G. Parr, J. Chem. Phys. **69**, 4431 (1978).