PHYSICAL REVIEW A **80**, 022506 (2009)

Quantal density-functional theory of the density amplitude: Application to atoms

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(Received 8 May 2009; published 14 August 2009)

Local effective potential theory of electronic structure is the mapping from a system of electrons in an external field to one of noninteracting fermions or bosons with the same electronic density. The energy and ionization potential are also thereby determined. The mappings may be achieved via either quantal density-functional theory (QDFT) or Hohenberg-Kohn-Sham density-functional theory (HKS-DFT). The wave function for the model fermionic system is a Slater determinant of spin orbitals, whereas that for the model bosons is the density amplitude. In the QDFT mappings, the contributions of the electron correlations due to the Pauli exclusion principle, Coulomb repulsion and correlation-kinetic effects are separately delineated. It has been proved via QDFT that the contribution of Pauli and Coulomb correlations to these model systems is the same; the difference lies solely in their correlation-kinetic component. In this paper, we apply the QDFT of the density amplitude to study the mapping to the bosonic model. The application is to atoms and performed at the Hartree-Fock theory level of electron correlations. A principal conclusion is that correlation-kinetic effects play a significant role in the mapping to the bosonic model, whereas they are negligible in the mapping to the model fermions. For the bosonic model, this contribution increases with electron number, becoming nearly as significant as those due to the corresponding electron-interaction (the sum of the Hartree and Pauli) term. The significance of the correlation-kinetic effects will be further enhanced on the inclusion of Coulomb correlations and the corresponding correlation-kinetic contributions. The consequences of these conclusions for the HKS-DFT of the density amplitude are discussed, as are directions for future work.

DOI: 10.1103/PhysRevA.80.022506 PACS number(s): 31.10.+z, 31.15.E−

I. INTRODUCTION

Ground-state local effective potential theory of electronic structure is the mapping from the ground state of a system of N electrons in an external field $\boldsymbol{\mathcal{F}}^{ext}(\mathbf{r})=-\boldsymbol{\nabla}v(\mathbf{r})$ to one of *noninteracting fermions* or *bosons* also in their ground state and with the same electronic density $\rho(\mathbf{r})$. The corresponding total energy E and ionization potential I are also thereby obtained via these model systems. (The models are referred to as the S and B systems, respectively.) Theories such as Hohenberg-Kohn-Sham density-functional theory [1,2] (HKS-DFT) and quantal density-functional theory [3] (QDFT) fall under the rubric of local effective potential theory. The *raison d'etre* for the mapping is that it is easier to solve the corresponding Schrödinger equation for the model systems than it is for the interacting system of electrons.

In order to ensure the same density $\rho(\mathbf{r})$, the model systems must account for electron correlations due to the Pauli exclusion principle and Coulomb repulsion. (We refer to these as Pauli and Coulomb correlations.) However, as the kinetic energy of the electrons and those of the noninteracting model particles with the same density are different, the model systems must also account for this correlation contribution to the kinetic energy. These are the correlation-kinetic contributions. As the model system particles (fermions or bosons) are noninteracting, their potential energy in each case is the same. As a consequence, all the above many-body effects are represented by a *local* (multiplicative) effective potential-energy operator $v_s(\mathbf{r})$ and $v_B(\mathbf{r})$ in the corresponding Schrödinger equations for the S and B systems, respectively. These effective potentials are in general different. It is the multiplicative nature of these many-body potentials that allow for an easier solution of the respective Schrödinger equations.

For the S system in its ground state, the occupation of states by the model fermions is according to the Pauli principle. The corresponding wave function Ψ_S is a Slater determinant $\Phi\{\phi_i\}$ of the N single-particle orbitals $\phi_i(\mathbf{x})$, where $\mathbf{x}=(\mathbf{r}\sigma)$ with $(\mathbf{r}\sigma)$ being the spatial and spin coordinates of the model fermion. The S system Schrödinger equation must then be solved self-consistently N times to obtain the wave function Ψ_S. The highest-occupied eigenvalue ϵ_m of the differential equation is the negative of the ionization potential I [3–6]. In contrast, for the B system, all the noninteracting bosons are in the same ground state. The corresponding wave function $\Psi_B=\sqrt{\rho(\mathbf{r})/N}$ and, thus, the solution of the B system Schrödinger equation leads directly to the density amplitude $\sqrt{\rho(\mathbf{r})}$. This differential equation needs to be solved only *once* to obtain the density $\rho(\mathbf{r})$. The single eigenvalue μ is the negative of the ionization potential I [5]. (For details of the different derivations of this result, we refer the reader to Chap. 6 of [3].) Most present day calculations of electronic structure involve the construction of approximate model S systems. However, the fact that in the mapping to the B system only one self-consistent solution is required to obtain the density is a considerable advantage. The focus of this paper, therefore, is to better understand the mapping to the model system of bosons. [Note that the B system may equally well be thought of as a single particle (fermion or boson) with wave function Ψ_B.]

The mapping to the S and B systems within the framework of HKS-DFT is in terms of universal energy functionals of the density in which all the above many-body effects are embedded. How these electron correlations are incorporated in these energy functionals is, however, not described by the theory. The effective potentials of the model particles are in turn defined as the corresponding functional derivatives of these energy functionals.

The QDFT [3] description of the *S* and *B* systems is in terms of "classical" fields and their quantal sources. The fields are separately representative of the contributions of electron correlations due to the Pauli principle, Coulomb repulsion, and correlation-kinetic effects. The effective potentials are then obtained as the work done in the force of a conservative field, which is the sum of the individual fields. The components of the total energy are in turn expressed in integral virial form in terms of these separate fields. As a consequence of this delineation, it is then possible to study the contributions of each type of electron correlation to a property of interest. Furthermore, it has been proved [3] via QDFT that the contributions of the Pauli and Coulomb correlations to both the *S* and *B* systems are the same. Thus, the difference between the two model systems is *solely* due to the difference in the correlation-kinetic contributions.

The principal thrust of this paper is to study the mapping to the *B* system of noninteracting bosons within the framework of QDFT [3] as applied to atoms. As there has been prior application to atoms of the QDFT mapping to the *S* system, it is then possible to make comparisons of the two mappings within QDFT. In Sec. II we describe the interacting system and provide the equations for the corresponding QDFT mapping to the *B* system with the same density $\rho(\mathbf{r})$. For details of the proof of this mapping as well as that for the QDFT mapping to the *S* system, we refer the reader to [3].

If the interacting system of electrons is described instead by the Hartree-Fock [7,8] or Hartree [9] theory, it is then also possible to map these systems via QDFT to model *B* systems that would reproduce the corresponding ground-state densities and energies. In Sec. III we study the QDFT mapping to the *B* system at the Hartree-Fock theory level of electron correlations as applied to the Be and Mg atoms. A comparison of these results with the QDFT description of the corresponding *S* system for these atoms [10] is made in Sec. IV. In Sec. V we discuss the consequences of our analysis and conclusions for the HKS-DFT of the *B* system. Conclusions and endnotes constitute Sec. VI.

For completeness we note that a description of the different derivations of the Schrödinger equation for the *B* system, and the corresponding expressions for the many-body potential $v_B(\mathbf{r})$ and the energy E, as derived in the context of the Hohenberg-Kohn theory, or directly from the Schrödinger equation for the electrons [5,11–15], is given in Chap. 6 of [3]. For additional work on the properties of the *B* system, see, for example, [16,17].

II. QDFT OF THE DENSITY AMPLITUDE

Consider a system of N electrons in an external field $\boldsymbol{\mathcal{F}}^{ext}(\mathbf{r})$ such that $\boldsymbol{\mathcal{F}}^{ext} = -\boldsymbol{\nabla} v(\mathbf{r})$. The electrons could be in their ground or excited state. The time-independent Schrödinger equation for this system is

$$\hat{H}\Psi(\mathbf{X}) = E\Psi(\mathbf{X}), \tag{1}$$

where the Hamiltonian in atomic units $\hat{H} = \hat{T} + \hat{V} + \hat{U}$, the sum of the kinetic, external potential, and electron-interaction potential operators, respectively: $\hat{T} = -\frac{1}{2}\Sigma_i \nabla_i^2$; $\hat{V} = \Sigma_i v(\mathbf{r}_i)$; $\hat{U} = \frac{1}{2}\Sigma'_{i,j} 1/|\mathbf{r}_i - \mathbf{r}_j|$. The energy is E, and the wave function $\Psi(\mathbf{X})$, where $\mathbf{X} = \mathbf{x}_1, \ldots, \mathbf{x}_N$ with $\mathbf{x} = \mathbf{r}\sigma$. The density $\rho(\mathbf{r})$ is the expectation

$$\rho(\mathbf{r}) = \langle \Psi(\mathbf{X}) | \hat{\rho}(\mathbf{r}) | \Psi(\mathbf{X}) \rangle, \tag{2}$$

where the Hermitian density operator

$$\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r}_i - \mathbf{r}). \tag{3}$$

The single-particle density matrix $\gamma(\mathbf{r}\mathbf{r}')$ is the expectation [3,18]

$$\gamma(\mathbf{r}\mathbf{r}') = \langle \Psi(\mathbf{X}) | \hat{\gamma}(\mathbf{r}\mathbf{r}') | \Psi(\mathbf{X}) \rangle, \tag{4}$$

where the density-matrix operator $\hat{\gamma}(\mathbf{r}\mathbf{r}')$ is the complex sum of the Hermitian operators $\hat{A}$ and $\hat{B}$,

$$\hat{\gamma}(\mathbf{r}\mathbf{r}') = \hat{A} + i\hat{B}, \tag{5}$$

where

$$\hat{A} = \frac{1}{2}\sum_j [\delta(\mathbf{r}_j - \mathbf{r})T_j(\mathbf{a}) + \delta(\mathbf{r}_j - \mathbf{r}')T_j(-\mathbf{a})], \tag{6}$$

$$\hat{B} = -\frac{i}{2}\sum_j [\delta(\mathbf{r}_j - \mathbf{r})T_j(\mathbf{a}) - \delta(\mathbf{r}_j - \mathbf{r}')T_j(-\mathbf{a})], \tag{7}$$

$T_j(\mathbf{a})$ is a translation operator such that $T_j(\mathbf{a})\Psi(\ldots,\mathbf{r}_j,\ldots) = \Psi(\ldots,\mathbf{r}_j+\mathbf{a},\ldots)$, and $\mathbf{a} = \mathbf{r}' - \mathbf{r}$. The diagonal matrix element $\gamma(\mathbf{r}\mathbf{r})$ is the density $\rho(\mathbf{r})$. The properties $\rho(\mathbf{r})$ and $\gamma(\mathbf{r}\mathbf{r}')$ constitute quantal sources.

The *B* system Schrödinger equation that reproduces the above density is

$$\left[-\frac{1}{2}\nabla^2 + v_B(\mathbf{r})\right]\sqrt{\rho(\mathbf{r})} = \mu\sqrt{\rho(\mathbf{r})}, \tag{8}$$

where the effective potential $v_B(\mathbf{r})$ of the bosons is

$$v_B(\mathbf{r}) = v(\mathbf{r}) + v_{ee}^B(\mathbf{r}), \tag{9}$$

and where $v_{ee}^B(\mathbf{r})$ is the local potential in which all the many-body effects are incorporated.

Within QDFT, $v_{ee}^B(\mathbf{r})$ is the work done to move a model boson from a reference point at infinity to its position at $\mathbf{r}$ in the force of a conservative effective field $\boldsymbol{\mathcal{F}}_B^{eff}(\mathbf{r})$,

$$v_B(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \boldsymbol{\mathcal{F}}_B^{eff}(\mathbf{r}') \cdot d\boldsymbol{\ell}'. \tag{10}$$

This work done is path independent since $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{F}}_B^{eff}(\mathbf{r}) = 0$. The effective field $\boldsymbol{\mathcal{F}}_B^{eff}(\mathbf{r})$ is the sum of the electron-interaction $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ and correlation-kinetic $\boldsymbol{\mathcal{Z}}_{t_c}^B(\mathbf{r})$ fields,

$$\boldsymbol{\mathcal{F}}_B^{eff}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{t_c}^B(\mathbf{r}). \tag{11}$$

The field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ accounts for electron correlations due to the Pauli principle and Coulomb repulsion and is given in terms of the electron-interaction force $\mathbf{e}_{ee}(\mathbf{r})$ and density as

$$\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) = \frac{\mathbf{e}_{ee}(\mathbf{r})}{\rho(\mathbf{r})}. \tag{12}$$

The force $\mathbf{e}_{ee}(\mathbf{r})$ is in turn obtained via Coulomb's law from the pair-correlation function $P(\mathbf{rr}')$, its quantal source

$$\mathbf{e}_{ee}(\mathbf{r}) = \int \frac{P(\mathbf{rr}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}', \tag{13}$$

with $P(\mathbf{rr}')$ the expectation

$$P(\mathbf{rr}') = \langle \Psi(\mathbf{X}) | \hat{P}(\mathbf{rr}') | \Psi(\mathbf{X}) \rangle, \tag{14}$$

where the Hermitian pair-correlation operator $\hat{P}(\mathbf{rr}')$ is

$$P(\mathbf{rr}') = \sum_{i,j}{}' \delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{r}_j - \mathbf{r}'). \tag{15}$$

[The ratio $P(\mathbf{rr}')/\rho(\mathbf{r}) = g(\mathbf{rr}')$ is the pair-correlation density, which satisfies the charge sum rule $\int g(\mathbf{rr}')d\mathbf{r}' = N-1$.]

The field $\boldsymbol{\mathcal{Z}}_{t_c}^{B}(\mathbf{r})$ representative of correlation-kinetic effects is the difference of two kinetic fields $\boldsymbol{\mathcal{Z}}_B(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}(\mathbf{r})$ of the model boson and interacting electron systems, respectively,

$$\boldsymbol{\mathcal{Z}}_{t_c}^{B}(\mathbf{r}) = \boldsymbol{\mathcal{Z}}_B(\mathbf{r}) - \boldsymbol{\mathcal{Z}}(\mathbf{r}), \tag{16}$$

where

$$\boldsymbol{\mathcal{Z}}_B(\mathbf{r}) = \frac{\mathbf{z}_B(\mathbf{r};\gamma_B)}{\rho(\mathbf{r})}, \quad \boldsymbol{\mathcal{Z}}(\mathbf{r}) = \frac{\mathbf{z}(\mathbf{r};\gamma)}{\rho(\mathbf{r})}. \tag{17}$$

The B system kinetic "force" $\mathbf{z}_B(\mathbf{r};\gamma_B)$ is defined in terms of the corresponding kinetic-energy-density tensor $t_{B,\alpha\beta}(\mathbf{r})$ as

$$z_{B,\alpha}(\mathbf{r}) = 2\sum_{\beta} \frac{\partial}{\partial r_\beta} t_{B,\alpha\beta}(\mathbf{r};\gamma_B), \tag{18}$$

with

$$t_{B,\alpha\beta}(\mathbf{r}) = \frac{1}{4}\left[\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha}\right]\gamma_B(\mathbf{r}'\mathbf{r}'')\big|_{\mathbf{r}'=\mathbf{r}''=r}, \tag{19}$$

and where the boson system density-matrix $\gamma_B(\mathbf{rr}')$ quantal source is

$$\gamma_B(\mathbf{rr}') = \sqrt{\rho(\mathbf{r})}\sqrt{\rho(\mathbf{r}')}. \tag{20}$$

The kinetic "force" $\mathbf{z}(\mathbf{r};\gamma)$ is defined similarly in terms of the interacting system density-matrix $\gamma(\mathbf{rr}')$ quantal source.

The total energy E of the electrons can then be obtained from the B system as the sum of the kinetic energy T_B of the bosons, the external energy E_{ext}, the electron-interaction energy E_{ee}, and the correlation-kinetic T_c^B energy,

$$E = T_B + E_{ext} + E_{ee} + T_c^B, \tag{21}$$

where

$$T_B = \int \sqrt{\rho(\mathbf{r})}\left(-\frac{1}{2}\nabla^2\right)\sqrt{\rho(\mathbf{r})}d\mathbf{r}, \tag{22}$$

$$E_{ext} = \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}, \tag{23}$$

and in integral virial form in terms of the respective fields,

$$E_{ee} = \int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})d\mathbf{r}, \tag{24}$$

$$T_c^B = \frac{1}{2}\int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{Z}}_{t_c}^{B}(\mathbf{r})d\mathbf{r}. \tag{25}$$

(The energies T_B and E_{ext} are given in traditional form. They may, however, also be written in terms of fields [3].) The expressions for E_{ee} and T_c^B are independent of whether the fields $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_{t_c}^{B}(\mathbf{r})$ are conservative or not.

Equations (10) and (21) constitute the QDFT mapping to the B system. Note that these equations are valid for the mapping from both the ground and excited states of the interacting system. Irrespective of the state of the interacting system, the B system is always constructed to be in its ground state.

The single eigenvalue μ of the B system differential equation is the negative of the ionization potential: $\mu = -I$ [5] (see also Chap. 6 of [3]).

As noted previously, the effective field $\boldsymbol{\mathcal{F}}_B^{eff}(\mathbf{r})$ is conservative. Its components $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_{t_c}^{B}(\mathbf{r})$ are in general not curl free. However, for systems of symmetry such that $\boldsymbol{\nabla}\times\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) = 0$ and $\boldsymbol{\nabla}\times\boldsymbol{\mathcal{Z}}_{t_c}^{B}(\mathbf{r}) = 0$, the potential energy $v_{ee}^B(\mathbf{r})$ may be written as

$$v_{ee}^B(\mathbf{r}) = W_{ee}(\mathbf{r}) + W_{t_c}^B(\mathbf{r}), \tag{26}$$

where $W_{ee}(\mathbf{r})$ and $W_{t_c}^B(\mathbf{r})$ are, respectively, the work done in the fields $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_{t_c}^{B}(\mathbf{r})$,

$$W_{ee}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}')\cdot d\boldsymbol{\ell}', \quad W_{t_c}^B(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{Z}}_{t_c}^{B}(\mathbf{r}')\cdot d\boldsymbol{\ell}'. \tag{27}$$

The work $W_{ee}(\mathbf{r})$ and $W_{t_c}(\mathbf{r})$ are separately path independent. [The field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ can be further divided into its Hartree $\boldsymbol{\mathcal{E}}_H(\mathbf{r})$ and Pauli-Coulomb $\boldsymbol{\mathcal{E}}_{xc}(\mathbf{r})$ components and, thus, so can the energy E_{ee} and potential $W_{ee}(\mathbf{r})$. The corresponding quantal sources are the density $\rho(\mathbf{r})$ and the Pauli-Coulomb hole charge distribution $\rho_{xc}(\mathbf{rr}')$ [3].]

Finally, the above framework of the mapping to the model boson system remains the same if the interacting system of electrons is represented at either the Hartree-Fock or Hartree theory level of electron correlation. The only difference in the QDFT equations is that the quantal sources $P(\mathbf{rr}')$ and $\gamma(\mathbf{rr}')$ are replaced by their Hartree-Fock and Hartree theory counterparts.

For the S system, the corresponding differential equation is

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\phi_i(\mathbf{x}) = \epsilon_i\phi_i(\mathbf{x}); \quad i = 1,\ldots,N, \tag{28}$$

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_{ee}(\mathbf{r}), \tag{29}$$

where all the many-body effects are incorporated in the potential $v_{ee}(\mathbf{r})$. The wave function is a Slater determinant $\Phi\{\phi_i\}$ of the orbitals $\phi_i(\mathbf{x})$, and the density is the expectation $\rho(\mathbf{r})=\langle\Phi\{\phi_i\}|\hat{\rho}(\mathbf{r})|\Phi\{\phi_i\}\rangle=\Sigma_{i,\sigma}\phi_i^*(\mathbf{r}\sigma)\phi_i(\mathbf{r}\sigma)$. Once again, the QDFT mapping to the S system involves an electron-interaction field component representative of Pauli and Coulomb correlations that is the *same* as in the B system, and a correlation-kinetic field component that is different. As no S system calculations are being performed in the present paper, we refer the reader to [3] for the corresponding equations of the QDFT mapping to this model system.

III. APPLICATION TO ATOMS

If the only electron correlations considered are those due to the Pauli exclusion principle, then the exact solution of the interacting system is that of Hartree-Fock theory. Exact fully self-consistent calculations for atoms in the Hartree-Fock approximation exist [19]. As described above, it is possible via the QDFT of the density amplitude to map to B systems that would reproduce the Hartree-Fock theory density and energy. In this section, we demonstrate this mapping for the spherically symmetric Be and Mg atoms.

Rather than use the self-consistent numerical orbitals of [19], we employ instead the analytical ground-state Hartree-Fock theory wave functions of Clementi and Roetti [20]. Thus, the mapping is from the *ground* state of the "interacting" system to a B system in its *ground* state. (The word interacting is in quotes to indicate that the correlations between the electrons are those due to the Pauli exclusion principle.)

It has been shown [21] that the B system is a special case of the S system. Now for the S system, it has been proved [21–23] that the S system electron-interaction potential $v_{ee}(\mathbf{r})$ counterpart of $v_{ee}^B(\mathbf{r})$ is finite at the nucleus. This is a consequence of the cusp in the wave function of the interacting system at the nucleus [24]. In terms of the density, the electron-nucleus coalescence condition to leading order is [21–23,25]

$$\rho(\mathbf{r})_{\mathbf{r}\to\infty} \sim \rho(0)(1-2Zr), \tag{30}$$

where Z is the atomic number. The fully self-consistent Hartree-Fock theory wave functions satisfy the electron-nucleus cusp condition exactly. For the analytical Hartree-Fock theory wave functions, the satisfaction of the coalescence condition is essentially exact. The corresponding relations for Be and Mg for these analytical wave functions are

$$\text{Be:}\quad \rho(\mathbf{r})_{\mathbf{r}\to\infty} \sim 35.4277(1-8.0389r), \tag{31}$$

$$\text{Mg:}\quad \rho(\mathbf{r})_{\mathbf{r}\to\infty} \sim 1093.7310(1-24.0228r). \tag{32}$$

With the analytical Hartree-Fock theory wave functions, the quantal sources—the Hartree-Fock theory density $\rho^{HF}(\mathbf{r})$, pair-correlation density $g^{HF}(\mathbf{r}\mathbf{r}')=P^{HF}(\mathbf{r}\mathbf{r}')/\rho^{HF}(\mathbf{r})$, Dirac density matrix $\gamma^{HF}(\mathbf{r}\mathbf{r}')$, and the bosonic system density matrix $\gamma_B^{HF}(\mathbf{r}\mathbf{r}')$—are first determined. (The superscript HF is dropped in the remainder of the paper.)

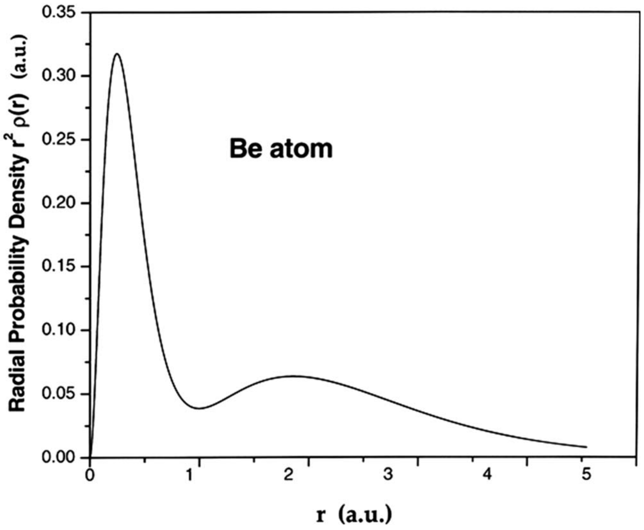

FIG. 1. The Hartree-Fock theory radial probability density of the Be atom.

The radial probability density $r^2\rho(r)$ of the Be atom is plotted in Fig. 1. The separately conservative electron-interaction $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ and correlation-kinetic $\boldsymbol{\mathcal{Z}}_{t_c}^B(\mathbf{r})$ fields for Be are plotted in Fig. 2. Observe that both the fields exhibit the two-shell structure of the atom. The field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ is positive and has a larger magnitude in the K shell. This field decays as $3/r^2$ asymptotically. This is because the quantal source $g(\mathbf{r}\mathbf{r}')$ of the field, which has a total charge of 3 a.u., becomes an essentially static charge distribution for asymptotic positions of the electron.

The correlation-kinetic field $\boldsymbol{\mathcal{Z}}_{t_c}^B(\mathbf{r})$ (see Fig. 2) is negative in the K shell and positive in the L shell. It is interesting that the magnitudes of the minimum and maximum are greater than that of the electron-interaction field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ in the K and L shells, respectively. However, the field $\boldsymbol{\mathcal{Z}}_{t_c}^B(\mathbf{r})$ decays as a positive function more rapidly in the asymptotic classically forbidden region than the electron-interaction field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$, which decays as $3/r^2$.

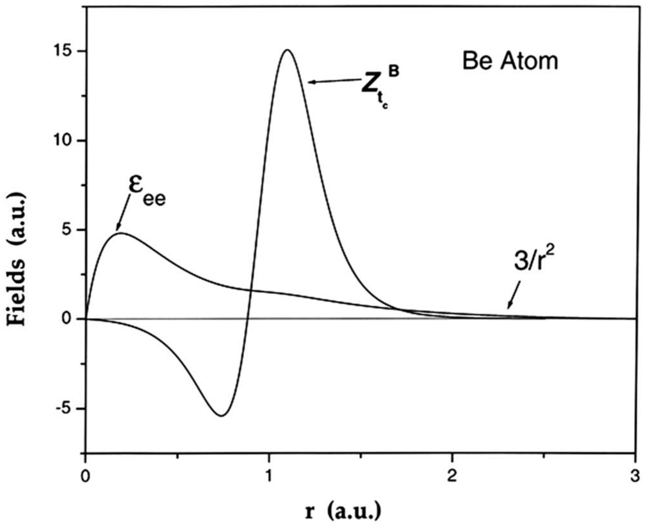

FIG. 2. The electron-interaction $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ and correlation-kinetic $\boldsymbol{\mathcal{Z}}_{t_c}^B(\mathbf{r})$ fields of the B system for the Be atom.

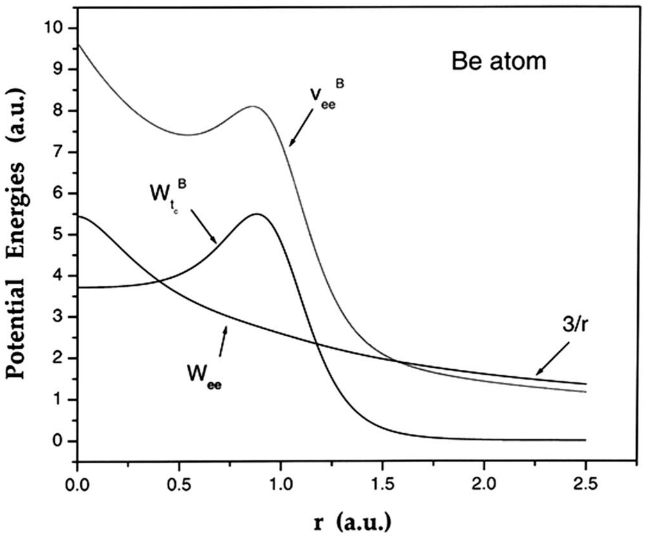

FIG. 3. The potential energies $W_{ee}(\mathbf{r})$, $W_{t_c}^B(\mathbf{r})$, and $v_{ee}^B(\mathbf{r})$ of the B system for the Be atom.

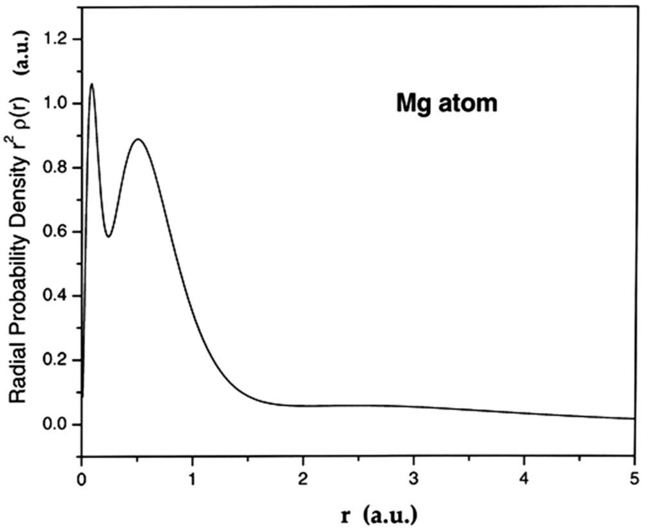

FIG. 4. The Hartree-Fock theory radial probability density of the Mg atom.

The work done $W_{ee}(\mathbf{r})$ and $W_{t_c}^B(\mathbf{r})$ in the fields $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathcal{Z}_{t_c}^B(\mathbf{r})$, respectively, and the work $v_{ee}^B(\mathbf{r})$ in the effective field $\mathcal{F}_B^{eff}(\mathbf{r})$ are plotted in Fig. 3. Observe first that $v_{ee}^B(\mathbf{r})$ is finite at the nucleus, a direct consequence of the electron-nucleus coalescence constraint on the wave function. The two-shell structure of the Be atom is evident in the potential $W_{t_c}^B(\mathbf{r})$. Asymptotically, this work decays more rapidly than $W_{ee}(\mathbf{r})$ which in turn decays as $3/r$. On the scale of the figure, the shell structure exhibited by $W_{ee}(\mathbf{r})$ is not that clearly visible. However, the shell structure is clearly exhibited by the structure of the potential energy $v_{ee}^B(\mathbf{r})$. Asymptotically, the curves of $W_{ee}(\mathbf{r})$ and $v_{ee}^B(\mathbf{r})$ merge, both decaying as $3/r$. Thus, the effective potential energy $v_B(\mathbf{r})$ decays asymptotically as $-1/r$.

The B system properties for the Be atom, viz., the kinetic energy T_B, the correlation-kinetic energy T_c^B, the external potential energy E_{ext}, the electron-interaction energy E_{ee}, and the total energy E, as determined from the corresponding fields, as well as the eigenvalue μ, and the experimental ionization potential I are quoted in a.u. in Table I. The results indicate the following. The correlation-kinetic-energy T_c^B component is 6.3% of the total energy E or, equivalently, of the (Hartree-Fock theory) kinetic energy T of the interacting system. The electron-interaction energy E_{ee} in turn is 31% of E. Thus, in the mapping to the B system, the correlation-kinetic contribution is significant. (That this is the case is more dramatically demonstrated in the results for the Mg atom to be discussed below.) The eigenvalue μ differs by 10% from the experimental result [26].

TABLE I. Properties of the B system for the Be and Mg atoms in a.u.

	Atom	
Property	Be	Mg
T_B	13.6587	132.5942
T_c^B	0.9143	67.0204
E_{ext}	−33.6647	−479.0672
E_{ee}	4.5186	79.8423
E	−14.5730	−199.6146
μ	0.3077	0.3968
I(experiment)	−0.3425	−0.2810

The B system results for Mg are presented as follows: the radial probability density $r^2\rho(r)$ is plotted in Fig. 4; the electron-interaction $\mathcal{E}_{ee}(\mathbf{r})$ and correlation-kinetic $\mathcal{Z}_{t_c}^B(\mathbf{r})$ fields in Figs. 5 and 6; the work done $W_{ee}(\mathbf{r})$ and $W_{t_c}^B(\mathbf{r})$ in the fields $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathcal{Z}_{t_c}^B(\mathbf{r})$, respectively, and the work $v_{ee}^B(\mathbf{r})$ in the effective field $\mathcal{F}_B^{eff}(\mathbf{r})$ are plotted in Fig. 7; the values of the properties T_B, T_c^B, E_{ext}, E_{ee}, E, μ, and the experimental I in Table I.

Once again, the potential $v_{ee}^B(\mathbf{r})$ is finite at the nucleus as must be the case. The three-shell structure of the Mg atom

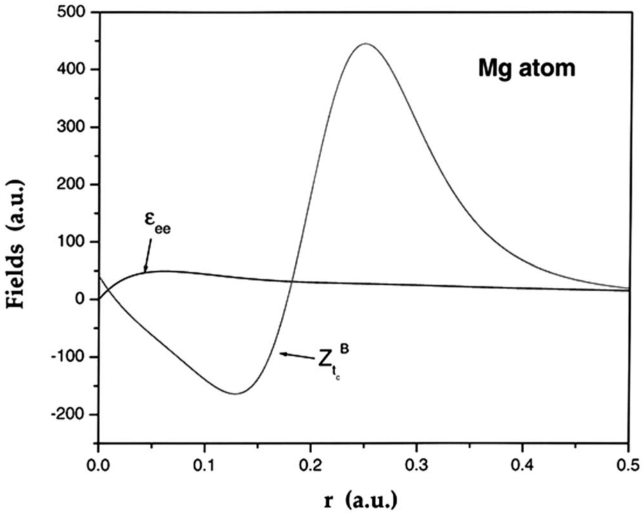

FIG. 5. The electron-interaction $\mathcal{E}_{ee}(\mathbf{r})$ and correlation-kinetic $\mathcal{Z}_{t_c}^B(\mathbf{r})$ fields of the B system for the Mg atom.

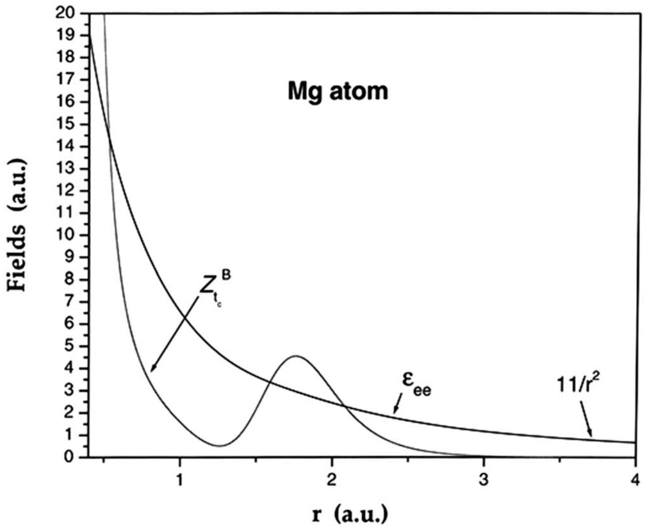

FIG. 6. The electron-interaction $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ and correlation-kinetic $\boldsymbol{\mathcal{Z}}_{t_c}^{B}(\mathbf{r})$ fields of the B system for the Mg atom in the classically forbidden region.

(see Fig. 4 for the radial probability density) is clearly evident in the plots for the correlation-kinetic field $\boldsymbol{\mathcal{Z}}_{t_c}^{B}(\mathbf{r})$ (see Figs. 5 and 6). Observe that the magnitude of the field $\boldsymbol{\mathcal{Z}}_{t_c}^{B}(\mathbf{r})$ is substantially larger than the field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ (see Fig. 5), but again decays asymptotically much faster than $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) \sim 11/r^2$. On the scale of Fig. 7, the shell structure is also evident in that of the potential energy $W_{t_c}^{B}(\mathbf{r})$ and, as expected, it decays asymptotically faster than $W_{ee}(\mathbf{r}) \sim 11/r$. The potential energy $v_{ee}^{B}(\mathbf{r})$ also exhibits the shell structure and decays as the potential energy $W_{ee}(\mathbf{r})$ (see Fig. 7). Thus, the B system effective potential energy $v_B(\mathbf{r})$ for Mg again decays asymptotically as $-1/r$.

The trends observed for the bosonic system properties for the Be atom are magnified for those of Mg (see Table I), i.e., with an increase in the number of electrons. For Mg, the correlation-kinetic energy T_c^B constitutes 34% of the total energy E, whereas the electron-interaction energy E_{ee} is 40% of E. Furthermore, the eigenvalue μ differs from the experimental ionization potential by 41%.

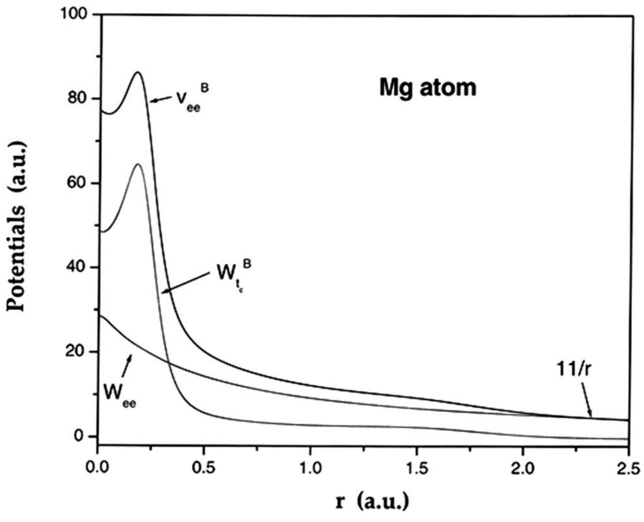

FIG. 7. The potential energies $W_{ee}(\mathbf{r})$, $W_{t_c}^{B}(\mathbf{r})$, and $v_{ee}^{B}(\mathbf{r})$ of the B system for the Mg atom.

The B systems described above reproduce the Hartree-Fock theory density and energy of the Be and Mg atoms. The potential energy $v_B(\mathbf{r})$ obtained from the various fields generates the density amplitude $\sqrt{\rho(\mathbf{r})}$ via Eq. (8), and the energy E and its components are obtained from these fields via Eq. (21).

IV. COMPARISON OF THE *B* AND *S* SYSTEMS

As noted in the introduction, the mapping to the B system requires the solution of a differential equation for a *single* orbital $\sqrt{\rho(\mathbf{r})}$, whereas for the mapping to a S system, the corresponding differential equation has to be solved for N orbitals, N being the number of electrons. The calculations of Sec. III, although performed at the Hartree-Fock theory level of correlation, indicate yet another significant difference between the two mappings. The corresponding correlation-kinetic contributions T_c of the S system and T_c^B of the B system differ substantially. In [10], S system calculations at the Pauli level of correlation were performed. The difference between the resulting energies and those of Hartree-Fock theory are an accurate estimate of the correlation-kinetic energy T_c. These differences for Be and Mg are 108 and 42 ppm, respectively. As noted above, the corresponding B system correlation-kinetic energies T_c^B for Be and Mg are 6% and 34% of the Hartree-Fock theory energy. Obviously, requiring the model noninteracting particles—bosons—to be in their ground state occupying a single state rather than allowing the model noninteracting particles—fermions—to be in their ground-state occupying states according to the Pauli exclusion principle is reflected in the correlation-kinetic component of the former being very much greater than that of the latter. It is reasonable to assume that this will also be the case when all the remaining correlations—those due to Coulomb repulsion and the corresponding correlation-kinetic contributions—are included in the mapping.

Note also that whereas for the S system at the Hartree-Fock level of correlation, with increasing number of electrons, the correlation-kinetic energy T_c diminishes (see [10]), the trend for the B system is the opposite. As the number of electrons increases, the correlation-kinetic piece T_c^B increases, thus, becoming a greater fraction of the total energy E.

Yet another comparison that can be made from the results obtained above is that between the highest-occupied eigenvalue ϵ_m of the S system and the eigenvalue μ of the B system. For the mappings when all the electron correlations are considered, both ϵ_m and μ are equivalent to the negative of the ionization potential I. However, at the approximate Hartree-Fock theory level of correlation, they are about the same for Be: ϵ_m and μ differ from the experimental values of I by 9% and 10%, respectively, but differ significantly for Mg. In this case, ϵ_m and μ differ from the experimental values of I by 7% and 41%, respectively (see [10] and Table I). Thus, with an increase in the number of electrons, the single eigenvalue μ is far less accurate. This is in spite of the fact that both the S and B system effective potential-energy functions $v_s(\mathbf{r})$ and $v_B(\mathbf{r})$ decay asymptotically as $-1/r$. With the incorporation of the Coulomb correlations and the remaining correlation-kinetic effects, the two eigenvalues ϵ_m and μ of course become equivalent.

V. CONSEQUENCES FOR TRADITIONAL DENSITY-FUNCTIONAL THEORY

The consequences of the above results and conclusions for traditional KS-DFT of the density amplitude (see [3]) are as follows. In the traditional theory, the mapping is from an interacting system in its *ground* state to one of noninteracting bosons in their ground state. The many-body effects of the Pauli principle, Coulomb repulsion, and the correlation-kinetic effects of the bosons are all incorporated in the ground-state electron-interaction energy functional $E_{ee}^B[\rho]$, with the potential $v_{ee}^B(\mathbf{r})$ being its functional derivative: $v_{ee}^B(\mathbf{r})=\delta E_{ee}^B[\rho]/\delta\rho(\mathbf{r})$ [3]. Since the functional $E_{ee}^B[\rho]$ is unknown, approximations to this functional are constructed with the physics of the various electron correlations being incorporated extrinsically. Now the QDFT derivations [3] of the B and S systems prove that the component due to Pauli and Coulomb correlations of the functional $E_{ee}^B[\rho]$ and of the Kohn-Sham electron-interaction energy functional $E_{ee}^{KS}[\rho]$ of the S system is the same. Thus, the approximate incorporation of these correlations into $E_{ee}^B[\rho]$ can be done in a manner similar to that presently being employed for the construction of S system approximate energy functionals $E_{ee}^{KS}[\rho]$. However, due the large magnitude of the correlation-kinetic effects for the bosonic system, the incorporation of these effects into the functional $E_{ee}^B[\rho]$ poses a difficult challenge. Unless these effects, which for bosonic systems are large, can be reasonably well accounted for in the functional $E_{ee}^B[\rho]$, the functional and its derivative will be inaccurate, and the KS-DFT of the density amplitude will then not lead to meaningful results.

VI. CONCLUSIONS AND ENDNOTES

In this paper, we have applied the QDFT of the density amplitude to atoms at the Hartree-Fock theory level of electron correlations. As such we have studied the mapping from this ground-state representation of the interacting system to the B system of noninteracting bosons in their ground state with the same density. The principal conclusion of this work is that in such a mapping, correlation-kinetic effects play a significant role, with its significance increasing with electron number. The correlation-kinetic contribution is a substantial fraction of the total energy; it also plays a role nearly as significant as that of the electron-interaction energy. This is in sharp contrast to the QDFT mapping to the S system model of noninteracting fermions with equivalent density in their ground state. For the latter, correlation-kinetic effects at this level of electron correlation are negligible.

It is evident that with the incorporation of Coulomb correlations into the mapping to the B system, correlation-kinetic effects will be even more significant. Work investigating these additional correlation-kinetic contributions is in progress. Studies of few electron atoms show that in the mapping to S systems, correlation-kinetic contributions to the total energy are on the same order of magnitude as that of Coulomb correlations. For two-electron systems, such as the Hooke's atom, the helium atom, and the hydrogen molecule in their ground state, the mappings to the S and B systems in a ground state are equivalent. For a quantitative comparison of the correlation-kinetic and Coulomb correlation contributions for these two-electron systems, see [3,27,28]. For the mapping from an *excited* state of the Hooke's atom to a B (or S) system in its ground state, see [3].

As noted previously, it has been shown [21,22] that the B and S system electron-interaction potentials $v_{ee}^B(\mathbf{r})$ and $v_{ee}(\mathbf{r})$, respectively, are finite at the nucleus. It is also shown that all the electron correlations—Pauli, Coulomb, and correlation kinetic—contribute to this value, i.e., to $v_{ee}^B(0)$ and $v_{ee}(0)$.

The asymptotic near nucleus structure of $v_{ee}(\mathbf{r})$ for spherically symmetric or sphericalized systems is of the form [22,23]

$$v_{ee}(\mathbf{r}) = \alpha + \beta r + \gamma r^2. \tag{33}$$

It has also been proved [23] via QDFT that (a) correlations due to the Pauli principle and Coulomb repulsion do not contribute to the linear structure; (b) these Pauli and Coulomb correlations contribute quadratically; and (c) the coefficient β is *solely* due to correlation-kinetic effects. The coefficient β of the linear term has been determined [23,29]. As the contribution of Pauli and Coulomb correlations to the S and B systems is the same, it is evident that the near nucleus structure of $v_{ee}^B(\mathbf{r})$ must be of the form

$$v_{ee}^B(\mathbf{r}) = \delta + \nu r + \kappa r^2, \tag{34}$$

with these correlations contributing to the coefficient κ of the quadratic term. The coefficient ν of the linear term, due solely to correlation-kinetic effects, is at present unknown and may be determined along the lines of [23,29].

Finally, it has also been shown [30,31] via QDFT that the asymptotic structure of $v_{ee}(\mathbf{r})$ in the classically forbidden region of spherically symmetric and sphericalized systems is of the form

$$v_{ee}(\mathbf{r}) = \frac{N}{r} - \frac{1}{r} - \frac{\alpha}{2r^4} + \frac{\kappa}{r^5}, \tag{35}$$

In this expression, the first term is the Hartree or Coulomb self-energy contribution; the second term is solely due to Pauli correlations; the term of $O(1/r^4)$ is solely due to Coulomb correlations with α the polarizability; the term of $O(1/r^5)$ is solely due to correlation-kinetic effects with the coefficient κ known. (The first three terms have also been derived [6] via the concept of quasiparticle amplitudes. See [31] for comments on this work.) Again, because the contributions of Pauli and Coulomb correlations to the S and B systems are the same, it is evident that the asymptotic structure of $v_{ee}^B(\mathbf{r})$ must be of the form

$$v_{ee}^{B}(\mathbf{r}) = \frac{N}{r} - \frac{1}{r} - \frac{\alpha}{2r^4} + \text{higher-order terms}. \tag{36}$$

The higher-order correlation-kinetic contribution to this structure is unknown and may be determined along the lines of [30].

The above asymptotic structures for the electron-interaction potentials $v_{ee}(\mathbf{r})$ and $v_{ee}^{B}(\mathbf{r})$ in the classically forbidden region then lead to an asymptotic structure of the S and B system effective potentials $v_s(\mathbf{r})$ and $v_B(\mathbf{r})$ of $(-1/r)$. This is consistent with previous work [5], which proved that $v_s(\infty)=v_B(\infty)=0$.

We conclude by noting that although there has been prior work on the B system, more work needs to be done to fully understand this mapping. The present work within the framework of QDFT, which allows for an investigation in terms of the separate electron correlations, is a beginning.

ACKNOWLEDGMENTS

The work of X.-Y.P. was sponsored by the National Natural Science Foundation of China (Grant No. 10805029) and the K C Wong Magna Foundation in Ningbo University. The work of V.S. was supported in part by a grant from the Research Foundation of The City University of New York.

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