Multicomponent Density-Functional Theory for Electrons and Nuclei

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A multicomponent density-functional theory is developed for the combined system of electrons and nuclei. We construct approximate functionals for the electron-nuclear correlation energy and illustrate the theory by explicit calculations for the H_2^+ molecular ion.

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First-principles calculations based on density-functional theory (DFT) [1,2] have greatly contributed to our understanding of atoms, molecules, and solids. Traditional DFT, by its very nature, always involves the Born-Oppenheimer (BO) approximation: One calculates the electronic ground-state density corresponding to the electrostatic potential of clamped nuclei. In addition, the nuclear degrees of freedom are often treated classically. Nevertheless, there is a wealth of phenomena requiring a description where these limitations have to be overcome. Among those where the quantum nature of the nuclei is known to be important are, e.g., surface reactions of small molecules [3], solid hydrogen [4], or floppy molecules. The nonadiabatic coupling between the electronic and nuclear motion manifests itself in numerous and rather diverse phenomena ranging from the Jahn-Teller effect and the electron-phonon interaction with its various consequences, to the branching ratios of chemical reactions [5] and the strong-field dynamics of molecules exposed to high-intensity laser fields [6]. To deal with phenomena of this kind, we propose, in this Letter, a generalization of DFT to multicomponent systems (MCDFT) which treats both electrons and nuclei quantum mechanically and which, at the same time, includes the nonadiabatic coupling between electronic and nuclear motion. The focus will be on stationary systems; time-dependent situations will be discussed elsewhere.

We consider a system of N_e electrons with coordinates $\{\mathbf{r}_j\} \equiv \underline{\underline{\mathbf{r}}}$ and N_n nuclei with masses $M_1, \ldots, M_{N_n}$, charges $Z_1, \ldots, Z_{N_n}$, and coordinates denoted by $\{\mathbf{R}_\alpha\} \equiv \underline{\underline{\mathbf{R}}}$. Such a system is characterized by the Hamiltonian

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{W}_{nn} + \hat{W}_{ee} + \hat{W}_{en}\,, \qquad (1)$$

where the subscripts "e" and "n" refer to electrons and nuclei, respectively. $\hat{T}$ denotes the kinetic energy and $\hat{W}$ represents the bare Coulomb interactions between the particles. Note that no BO approximation has been assumed in (1); in particular, the Coulomb interaction between electrons and nuclei is not treated as an external potential. Truly external potentials representing, e.g., an applied voltage are easily included in the formalism. For the sake of simplicity we restrict ourselves, in this Letter, to the case of vanishing external fields.

As a first step towards the formulation of a MCDFT scheme, we discuss the choice of densities which will serve as the fundamental variables of the theory. One might be tempted to use the single-particle electronic density obtained from a solution $\Psi(\underline{\underline{\mathbf{R}}}, \underline{\underline{\mathbf{r}}})$ of the Schrödinger equation (SE) associated with the Hamiltonian (1): $\rho(\mathbf{r}) = N_e \int d^{N_n}\mathbf{R} \int d^{N_e-1}\mathbf{r}\, |\Psi(\underline{\underline{\mathbf{R}}}, \underline{\underline{\mathbf{r}}})|^2$ and an analogous quantity for the nuclei. A MCDFT is readily formulated in terms of these densities [7]. However, this MCDFT, although formally correct, is not useful in practice because the densities, as a consequence of the translational invariance of Hamiltonian (1), are constant for *all* isolated atoms, molecules, and solids and therefore are *not* characteristic of the internal properties of the system.

A suitable single-particle density is obtained by defining it with respect to a coordinate frame which is attached to the system. To this end, the electronic coordinates in (1) are transformed to a body-fixed frame according to $\mathbf{r}'_j := \mathcal{R}(\alpha, \beta, \gamma)(\mathbf{r}_j - \mathbf{R}_{\text{c.m.n.}})$, $j = 1, \ldots, N_e$, where $\mathbf{R}_{\text{c.m.n.}} := \frac{1}{M_{\text{nuc}}} \sum_\alpha M_\alpha \mathbf{R}_\alpha$ denotes the center of mass (c.m.) of the nuclei, $M_{\text{nuc}} := \sum_\alpha M_\alpha$, and $\mathcal{R}$ is the 3×3 orthogonal matrix representing the Euler rotations [8]. The Euler angles (α, β, γ) specify the orientation of the body-fixed coordinate frame and are determined by requiring the nuclear inertial tensor to be diagonal in the body-fixed frame. Of course, introducing internal nuclear coordinates appears desirable as well. However, the choice of such coordinates depends strongly on the specific system to be described: If near-equilibrium situations of systems with well-defined geometries are considered, normal or phonon coordinates are most appropriate, whereas fragmentation processes of molecules are better described in terms of Jacobi coordinates. Therefore, in order to keep a high degree of flexibility, the nuclear coordinates are left unchanged at this point and are only transformed prior to actual applications.

As a result of the above coordinate transformation, the kinetic-energy part of the Hamiltonian (1) transforms into (using atomic units)

$$\hat{T} = \sum_\alpha \left(-\frac{\nabla^2_{\mathbf{R}_\alpha}}{2M_\alpha}\right) + \sum_j \left(-\frac{\nabla^2_{\mathbf{r}'_j}}{2}\right) + \hat{T}_{\text{MPC}}\,. \qquad (2)$$

$\hat{T}_{\mathrm{MPC}} := \sum_\alpha (-\frac{1}{2M_\alpha})(\nabla_{\mathbf{R}_\alpha} + \sum_j \frac{\partial \mathbf{r}'_j}{\partial \mathbf{R}_\alpha} \nabla_{\mathbf{r}'_j})^2 - \hat{T}_n$ represents the mass polarization and Coriolis contributions arising from the transformation to a noninertial coordinate frame. In order to formulate a Hohenberg-Kohn–type statement, the Hamiltonian (1) is generalized to $\hat{H} = \hat{T} + \hat{W} + \hat{V}_n + \hat{V}_e$, where $\hat{W} = \hat{W}_{ee} + \hat{W}_{en}$ comprises the electron-electron and the electron-nuclear interactions, and where $\hat{V}_n = V_n(\underline{\underline{\mathbf{R}}})$ and $\hat{V}_e = \sum_j v_e(\mathbf{r}'_j)$ represent auxiliary "external" potentials referring to the transformed coordinates. $\hat{V}_n$ is an arbitrary multiplicative N_n-body operator with respect to the nuclear coordinates and includes the nuclear-nuclear interaction $\hat{W}_{nn}$. In terms of the ground-state wave function $\Psi(\underline{\underline{\mathbf{R}}}, \underline{\mathbf{r}}')$ of this Hamiltonian, we define the following densities:

$$\rho(\mathbf{r}') = N_e \int d^{N_n}\mathbf{R} \int d^{N_e - 1}\mathbf{r}' \, |\Psi(\underline{\underline{\mathbf{R}}}, \underline{\mathbf{r}}')|^2, \qquad (3)$$

$$\Gamma(\underline{\underline{\mathbf{R}}}) = \int d^{N_e}\mathbf{r}' \, |\Psi(\underline{\underline{\mathbf{R}}}, \underline{\mathbf{r}}')|^2. \qquad (4)$$

By Eq. (3), an electronic single-particle density is defined with respect to the body-fixed frame which is characteristic of the internal properties of the system. The nuclear degrees of freedom are described by the N_n-particle nuclear density matrix, given by Eq. (4).

The transformed Hamiltonian and the above defined densities (3) and (4) now provide a suitable basis for the formulation of a MC Hohenberg-Kohn (MCHK) theorem. It can be summarized by the following statements: (1) The set of ground-state densities $\{\Gamma, \rho\}$ uniquely determines the ground-state wave function, $\Psi = \Psi[\Gamma, \rho]$, as well as the set of potentials, $\{\hat{V}_n[\Gamma, \rho], \hat{V}_e[\Gamma, \rho]\}$. As a consequence, any observable of the static many-body system is a functional of the set of ground-state densities $\{\Gamma, \rho\}$. (2) The total-energy functional $E[\Gamma, \rho] := \langle \Psi[\Gamma, \rho] | \hat{H} | \Psi[\Gamma, \rho] \rangle$ is equal to the exact ground-state energy E_0 of the system only if the exact ground-state densities Γ_0 and ρ_0 are inserted. For all other densities, the inequality $E_0 < E[\Gamma, \rho]$ holds true. This MCHK theorem can be proven along the usual lines [2] using either the reductio ad absurdum or the constrained search approach.

As usual, the HK proof goes through for any particle-particle interaction. We can therefore apply it to an auxiliary system which is characterized by $\hat{W} \equiv 0$, i.e., it consists of noninteracting electrons and of nuclei which interact only among themselves. The ground state associated with this system is then described by

$$\left(-\frac{\nabla^2}{2} + v_{S,e}(\mathbf{r}) - \epsilon_{e,j}\right)\varphi_j(\mathbf{r}) = 0, \qquad (5)$$

$$\left(-\sum_\alpha \frac{\nabla_\alpha^2}{2M_\alpha} + V_{S,n}(\underline{\underline{\mathbf{R}}}) - \epsilon_n\right)\chi(\underline{\underline{\mathbf{R}}}) = 0, \qquad (6)$$

and the corresponding densities are given by

$$\rho(\mathbf{r}) = \sum_j |\varphi_j(\mathbf{r})|^2, \qquad \Gamma(\underline{\underline{\mathbf{R}}}) = |\chi(\underline{\underline{\mathbf{R}}})|^2. \qquad (7)$$

(For notational simplicity, the primes at the electronic coordinates are dropped from here on. By convention, all electronic coordinates are understood to refer to the body-fixed frame.) Assuming noninteracting—$\{V_n, v_e\}$—representability, the effective potentials $V_{S,n}(\underline{\underline{\mathbf{R}}})$ and $v_{S,e}(\mathbf{r})$ of the auxiliary system can be chosen such that (7) reproduces the exact ground-state densities $\{\Gamma_0, \rho_0\}$ of the fully interacting many-particle system. Once the existence of $V_{S,n}$ and $v_{S,e}$ is assumed, they are, by virtue of the MCHK theorem, uniquely defined by the ground-state densities. In fact, using the MCHK variational theorem, we obtain

$$v_{S,e}(\mathbf{r}) = v_e(\mathbf{r}) + v_{\mathrm{Hxc}}(\mathbf{r}), \qquad (8)$$

$$V_{S,n}(\underline{\underline{\mathbf{R}}}) = V_n(\underline{\underline{\mathbf{R}}}) + V_{\mathrm{Hxc}}(\underline{\underline{\mathbf{R}}}), \qquad (9)$$

where $V_n(\underline{\underline{\mathbf{R}}})$ and $v_e(\mathbf{r})$ are the external potentials introduced above. For isolated systems, $V_n(\underline{\underline{\mathbf{R}}})$ contains only the internuclear Coulomb repulsion, i.e., $V_n(\underline{\underline{\mathbf{R}}}) \equiv W_{nn}(\underline{\underline{\mathbf{R}}})$, and $v_e(\mathbf{r})$ vanishes. The Hartree-exchange-correlation (Hxc) potentials are defined as functional derivatives of the Hxc energy functional, i.e., $v_{\mathrm{Hxc}}(\mathbf{r}) := \delta E_{\mathrm{Hxc}}[\Gamma, \rho] / \delta\rho(\mathbf{r})_{\Gamma_0, \rho_0}$ and $V_{\mathrm{Hxc}}(\underline{\underline{\mathbf{R}}}) := \delta E_{\mathrm{Hxc}}[\Gamma, \rho] / \delta\Gamma(\underline{\underline{\mathbf{R}}})_{\Gamma_0, \rho_0}$. The Hxc energy functional represents the central quantity of MCDFT and is defined by

$$E_{\mathrm{Hxc}}[\Gamma, \rho] := F[\Gamma, \rho] - T_{S,n}[\Gamma] - T_{S,e}[n], \qquad (10)$$

where $T_{S,n}[\Gamma] = \int d^{N_n}\mathbf{R} \, \chi^\star(\underline{\underline{\mathbf{R}}}) \sum_\alpha [-\nabla_\alpha^2 / (2M_\alpha)] \chi(\underline{\underline{\mathbf{R}}})$ and $T_{S,e}[n] = \sum_j \int d\mathbf{r} \, \varphi_j^\star(\mathbf{r}) (-\nabla^2/2) \varphi_j(\mathbf{r})$ represent the kinetic energies of the auxiliary system and $F[\Gamma, \rho] = \langle \Psi[\Gamma, \rho] | \hat{T} + \hat{W} | \Psi[\Gamma, \rho] \rangle$. By definition, $E_{\mathrm{Hxc}}[\Gamma, \rho]$ contains all many-body effects except the nuclear repulsion, which is treated exactly within the auxiliary system.

Equations (5)–(9) constitute the MC Kohn-Sham (MCKS) system. Since the effective potentials depend on both densities, the electronic and the nuclear SE are coupled and have to be solved self-consistently. We emphasize that Eq. (5), although formally similar to the usual electronic KS equation, does *not* depend parametrically on the nuclear configurations. Instead, the information on the nuclear density distribution is included through the functional dependence on Γ. Considering the nuclear MCKS equation (6), we realize its similarity with the conventional nuclear BO equation. Yet, *no* BO approximation has been used to derive Eq. (6). Since the MCKS scheme provides the exact ground-state densities of the system, all non-BO effects are, in principle, included. Like the nuclear BO equation, Eq. (6) involves an N_n-body multiplicative potential. This is an immediate consequence of choosing the nuclear N_n-body density matrix Γ as a basic variable. Had we chosen the nuclear single-particle density instead of Γ, we would have obtained a 1-body SE in place of Eq. (6), and this would not have allowed for a realistic description of collective degrees of freedom such as phonons. Only by setting up the MCDFT in terms of $\Gamma(\underline{\underline{\mathbf{R}}})$ and the corresponding many-body SE (6), the formalism has sufficient flexibility to encompass a large variety of situations: For single molecules and solids, the nuclear many-body SE (6) will usually be treated within the harmonic approximation, leading to solutions in terms of normal or phonon modes. For liquids and plasmas, on the other hand, a Hartree-Fock–type treatment of Eq. (6) will be more appropriate.

For any practical application, the functional $E_{\text{Hxc}}[\Gamma,\rho]$ needs to be approximated. The remaining part of this Letter will be devoted to the construction of explicit approximations for E_{Hxc}. We first decompose the functional into parts associated with the different interactions: Following [9], we write

$$E_{\text{Hxc}}[\Gamma,\rho] = E_{\text{H}}^{e}[\rho] + E_{\text{xc}}^{e}[\rho] + E_{\text{Hc}}^{en}[\Gamma,\rho] + T_{\text{MPC}}[\Gamma,\rho], \tag{11}$$

where the first two terms are the familiar Hartree and xc energy functionals known from standard electronic DFT. It is important to note that the electron-electron interaction can therefore be treated in the usual way, namely, by employing the highly successful and well-studied approximations for $E_{\text{xc}}^{e}[\rho]$. The last term on the right-hand side of Eq. (11) includes all effects due to mass polarization and Coriolis forces. At least for ground-state properties, this term is expected to be very small. The third term in Eq. (11), $E_{\text{Hc}}^{en}[\Gamma,\rho]$, contains all effects due to the electron-nuclear interaction. Using the coupling-constant integration technique [10], adapted to the electron-nuclear interaction [9], it can be shown that

$$E_{\text{Hc}}^{en}[\Gamma,\rho] = \int d^{N_n}\mathbf{R}\,\Gamma(\underline{\underline{\mathbf{R}}}) \times \int d\mathbf{r}\, W_{en}(\mathbf{r},\underline{\underline{\mathbf{R}}})\bar{\gamma}[\Gamma,\rho](\mathbf{r}\,|\,\underline{\underline{\mathbf{R}}}), \tag{12}$$

where $W_{en}(\mathbf{r},\underline{\underline{\mathbf{R}}}) = -\sum_\alpha Z_\alpha/|\mathcal{R}^{-1}\mathbf{r} - \mathbf{R}_\alpha + \mathbf{R}_{\text{c.m.n.}}|$, and $\gamma(\mathbf{r}\,|\,\underline{\underline{\mathbf{R}}}) := N_e \int d^{N_e-1}\mathbf{r}\,|\Psi(\underline{\underline{\mathbf{R}}},\underline{\underline{\mathbf{r}}})|^2/\Gamma(\underline{\underline{\mathbf{R}}})$ denotes the electronic conditional density. $\bar{\gamma}$ represents the coupling-constant average of γ.

To gain further insight in the functional E_{Hc}^{en} we first consider the corresponding potentials in two limiting situations: If the nuclei are perfectly localized at $\underline{\underline{\mathbf{R}}}_{eq}$, it is easy to see that the potential $v_{\text{Hc}}^{en}(\mathbf{r})$ reduces to $W_{en}(\mathbf{r},\underline{\underline{\mathbf{R}}}_{eq})$, i.e., it coincides with the classical Coulomb field of the nuclei in ordinary BO-based DFT. Hence, in the limit of classical nuclei the MCDFT method reduces to the standard electronic DFT. Next, we turn our attention to the nuclear MCKS Eq. (6). If the BO approximation accurately describes the system under consideration, one can show that $V_{\text{Hxc}}(\underline{\underline{\mathbf{R}}}) \approx \epsilon_0^{\text{BO}}(\underline{\underline{\mathbf{R}}})$, where ϵ_0^{BO} denotes the lowest BO potential-energy surface. As a consequence, the nuclear MCKS equation reduces to the nuclear BO equation in this limit. We emphasize, however, that the way to evaluate this potential differs in the MCKS and BO methods. Whereas, in the latter, an electronic equation has to be solved for each nuclear configuration, the MCKS potential is determined by the *functional* derivative $\delta E_{\text{Hc}}^{en}[\Gamma,\rho]/\delta\Gamma(\underline{\underline{\mathbf{R}}})$. Inserting the ground-state densities then yields a potential which, in this particular case, is very close to the BO potential as a *function* of $\underline{\underline{\mathbf{R}}}$.

It remains to find approximations of the electron-nuclear Hartree-correlation (Hc) energy $E_{\text{Hc}}^{en}[\Gamma,\rho]$. The easiest approach replaces E_{Hc}^{en} by the Hartree energy

$$E_{\text{H}}^{en}[\Gamma,\rho] = \int d^{N_n}\mathbf{R} \int d\mathbf{r}\,\Gamma(\underline{\underline{\mathbf{R}}})W_{en}(\mathbf{r},\underline{\underline{\mathbf{R}}})\rho(\mathbf{r}). \tag{13}$$

In other words, the electron-nuclear interaction is approximated by the classical electrostatic interaction of the corresponding charge distributions [11] and correlation contributions are neglected. In order to assess the accuracy of this (crudest-possible) approximation, we apply it to the simplest diatomic molecule, namely, the H_2^+ molecular ion. Since there is no electron-electron interaction, this molecule naturally lends itself as a prototype for the analysis of the previously not much studied electron-nuclear correlation energy.

In order to solve the MCKS equations for the H_2^+ molecule, we first separate off the nuclear c.m. motion in Eq. (6) so that the remainder of χ depends only on the internuclear separation $R := |\mathbf{R}_2 - \mathbf{R}_1|$. Then, the remaining equations are treated numerically on a finite-difference grid. In the second column of Table I, we show a selection of results obtained within the Hartree approximation as described above. Since the H_2^+ molecule is well described within the BO approximation, we have also added the BO results in the first column of this table. Considering the simplicity of the Hartree approximation, we find surprisingly good results. Especially the total energy E_0 and the geometry, represented by the mean internuclear distance $\langle R\rangle$, are in good agreement with the exact results, with deviations of about 1%. However, turning towards the harmonic constant ω, we find that the Hartree result is off by more than a factor of 2. Comparing (13) with (12) we realize that the Hartree approximation corresponds

TABLE I. Comparison of results obtained for the H_2^+ molecules from self-consistent solutions of the MCKS scheme using the various approaches discussed in the text. For comparison, results from BO calculations are added. All numbers (except ω) are in atomic units.

	BO	Hartree	OAO	SAO
$-E_0$	0.598	0.591	0.595	0.581
T_S		0.591	0.583	0.574
$-E_{\text{Hc}}^{en}$		1.673	1.662	1.642
$\langle 1/R\rangle$	0.489	0.491	0.485	0.487
$\langle R\rangle$	2.07	2.05	2.08	2.08
$\langle R^2\rangle$	4.30	4.22	4.37	4.39
ω (cm^{-1})	2297	5191	3248	2232

to replacing the electronic conditional density $\bar{\gamma}(\mathbf{r}\,|\,R)$ by $\rho(\mathbf{r})$. This is a good approximation near R_{eq} but fails seriously for larger R. To improve on the Hartree functional, we approximate $\gamma(\mathbf{r}\,|\,R)$, in the spirit of the Heitler-London approach, by

$$\gamma(\mathbf{r}\,|\,R) \approx \frac{1}{\nu(R)} \times \left| \Phi\left(\mathbf{r} - \frac{R}{2}\mathbf{e}_z\right) + \Phi\left(-\mathbf{r} - \frac{R}{2}\mathbf{e}_z\right) \right|^2, \tag{14}$$

where the "atomic" orbital $\Phi(\mathbf{r})$ is to be represented as a functional of the densities: $\Phi = \Phi[\Gamma, \rho]$. To that end, we first recall the fact that, given an *atomic orbital* $\Phi(\mathbf{r})$, bonding and antibonding *molecular orbitals*—for a fixed internuclear distance R—can be obtained from

$$\psi_R^{B/A}(\mathbf{r}) = \frac{1}{\sqrt{\nu_\pm(R)}} \times \left[\Phi\left(\mathbf{r} - \frac{R}{2}\mathbf{e}_z\right) \pm \Phi\left(-\mathbf{r} - \frac{R}{2}\mathbf{e}_z\right) \right]. \tag{15}$$

$\nu(R)$ in Eq. (14) and $\nu_\pm(R)$ in (15) ensure normalization. To construct the functional $\Phi[\Gamma, \rho]$, we now identify the electronic MCKS orbitals, i.e., the solutions of Eq. (5) for the ground state, $\phi_0(r)$, and for the first excited state, $\phi_1(\mathbf{r})$, with the bonding/antibonding orbitals of Eq. (15) at $R = \langle R \rangle$, i.e., $\phi_{0/1}(\mathbf{r}) \equiv \psi_{\langle R \rangle}^{B/A}$. Using this prescription, we can solve Eq. (15) for the atomic orbital, which is therefore determined as an implicit functional of the densities Γ and n. Inserting the atomic orbital in (14) leads to an approximation for the conditional density and, by virtue of Eq. (13), to an approximation for $E_{\mathrm{Hc}}^{en}[\Gamma, \rho]$ as an (implicit) functional of the densities. The results obtained by applying this "optimized atomic orbital" (OAO) approximation to the H_2^+ molecule are presented in the third column of Table I. Apparently, the method consistently improves upon the Hartree approach. The total energy and the geometry are almost on top of the BO results, and the deviations in the harmonic constant ω are also somewhat reduced within the OAO approximation. However, the remaining error in ω is still substantial and can be explained by the wrong $R \to \infty$ asymptotics of $\gamma^{\mathrm{OAO}}(\mathbf{r}\,|\,R)$.

In view of the first successes of the OAO approach, we further exploit the ansatz (14) to include correlation contributions for the electron-nuclear interaction. However, in order to improve on the failures of the OAO approach, we slightly change the prescription of how to construct the atomic orbital $\Phi[\Gamma, \rho]$. Instead of employing Eq. (15), the atomic orbital Φ is now obtained by a scaling procedure [12]: $\Phi(\mathbf{r}) = \lambda^{3/2}\Phi_\infty(\lambda\mathbf{r})$. The scaling function $\lambda(R)$ is determined self-consistently as a functional of the densities, $\lambda(R) = \lambda[\Gamma, \rho](R)$, by employing the sum rule

$$\rho(\mathbf{r}) = \int dR\, \Gamma(R)\gamma(\mathbf{r}\,|\,R), \tag{16}$$

which is a rigorous property of the conditional density $\gamma(\mathbf{r}\,|\,R)$. Furthermore, choosing ϕ_∞ as the electronic KS orbital of the separated atomic limit ensures the correct behavior in the $R \to \infty$ limit. Although this "scaled atomic orbital" (SAO) approach slightly worsens the total energy of the H_2^+ molecule, as seen in the last column of Table I, the harmonic constant is now in very good agreement with the BO results.

In conclusion, we have presented a multicomponent DFT for the complete system of electrons and nuclei. The method is similar, in spirit, to the Car-Parrinello scheme [13] in that it avoids the calculation of BO surfaces while, at the same time, the nuclear degrees of freedom are treated fully quantum mechanically.

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