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Ground state of a hydrogen molecule in superstrong magnetic fields

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We study the ground-state structural properties of a hydrogen molecule in superstrong magnetic fields ($B\approx 10^{12}$ G) using quantum Monte Carlo (fixed-phase and variational) approaches. We determine that the ground state (spin-triplet) belongs to the sector of total (z-component) angular momentum $M=-1$ ($^3\Pi_0$), meaning that paramagnetic contributions to the total energy cannot be neglected. This non-time-reversal invariant ground state has a strong interatomic interaction, suggesting that a hydrogen gas under the same physical conditions has a tendency to form strong bonded molecules.

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What is the ground-state symmetry of a hydrogen molecule in a superstrong external magnetic field? This question and other related matters constitute the subject of this short communication. Recently [1] there has been some discussion on whether a hydrogen gas can become superfluid in the presence of a strong external magnetic field. The crucial argument [2] behind such a claim is that, due to weak interatomic interactions, the system behaves as a weakly interacting Bose gas and as a consequence of macroscopic exchanges it becomes superfluid. However, as has been pointed out by Lai [1], the system is strongly interacting, with a compelling tendency to forming a molecular phase before Bose-Einstein condensation takes place. The gist of the discrepancy lies in the assumption of different symmetries for the molecular ground states. We will show that the argument supporting a superfluid phase [2] is flawed, since, in agreement with Lai, the system is strongly bonded.

The properties and stability of matter under extreme conditions are of general interest due to their wide range of applications in different research areas, such as astrophysics, atomic, and condensed matter physics. With the discovery of pulsars and magnetized white dwarfs, the study of atomic [3] and molecular systems in strong magnetic fields has taken on a renewed importance. For many of these stars, the fields are strong enough to warrant a nonperturbative treatment. In particular, the surface of some neutron stars exhibits superintense field strengths ($B\approx 10^{12}$ G), which dramatically influence the structural and optical properties of matter. From the theoretical viewpoint, it is not clear whether a *mean-field* theory like Hartree-Fock is in principle able to capture the main physics of electron correlations, because of a nontrivial balance between coupled Lorentz and Coulomb forces. Moreover, most practical applications assume the *adiabatic approximation* [4], which amounts to retaining only the cylindrical symmetry imposed by the external field and which becomes asymptotically correct as $B\to\infty$. Consequently, in order to shed light on this issue one has to resort to many-body methods that are better suited to deal with strongly correlated fermions. Depending on the relative strength between Coulomb and Lorentz forces, we can characterize three different regimes: the low ($\gamma\leqslant 10^{-3}$), the intermediate ($10^{-3}\leqslant\gamma\leqslant 1$), and the superstrong ($\gamma\gg 1$) field regimes, where $\gamma=ea_0^2B/2\hbar c=B/B_0$ ($B_0=4.7\times 10^9$ G). It is the superstrong regime that is relevant for neutron star physics and is of interest to us in this paper.

To simplify matters we will assume the conventional Born-Oppenheimer adiabatic separation of electronic and nuclear motion, i.e., without including the effects of the non-Abelian Mead-Berry connection in the slow variables induced by the fast electronic motion [5]. Besides, we are not concerned with enforcing the correct permutational symmetry on the total wave function with respect to identical nuclei exchanges, and consider only the electron dynamics, which in turn depends parametrically on the nuclear space coordinates $\mathbf{R}_j$ ($j=1, 2$) (with internuclear separation R and axis whose center coincides with the origin of the coordinate reference frame).

Let us start by writing the nonrelativistic Hamiltonian that governs the dynamics of our two-fermion system in the Coulomb potential of two nuclei with infinite mass and charge Z and in the presence of an external electromagnetic potential $A_\mu=(\mathbf{A}(\mathbf{r}),0)$,

$$\hat{\mathscr{H}}=\sum_{i=1}^{2}\left[\frac{[\sigma_i\cdot\mathbf{\Pi}_i]^2}{2m}-\sum_{j=1}^{2}\frac{Ze^2}{R_{ij}}\right]+\frac{e^2}{r_{12}}+\frac{Z^2e^2}{R}\ , \qquad (1)$$

where σ_i^k, $k=1, 2, 3$ denote the Pauli spin matrices, $\mathbf{r}_i$ represents the electron vector position, $R_{ij}=|\mathbf{r}_i-\mathbf{R}_j|$, and $\mathbf{\Pi}_i=\mathbf{p}_i+(e/c)\mathbf{A}(\mathbf{r}_i)$ is the kinetic momentum. The first term in Eq. (1) is the Pauli kinetic energy and is the nonrelativistic approximation to the Dirac operator. Hence, we are dealing with spin-$\frac{1}{2}$ fermions of mass m and charge $-e$, coupled, in principle, to both orbital and spin degrees of freedom (Zeeman term). Notice that, for simplicity, we have not considered spin-orbit coupling.

To simplify our calculations and analysis of symmetries we choose the symmetric gauge for $\mathbf{A}[\mathbf{A}_s=B/2(-y, x, 0)]$. Then, in Hartree atomic units, the Hamiltonian reads

$$\hat{\mathscr{H}}=\sum_{i=1}^{2}\left[-\frac{\nabla_i^2}{2}-\sum_{j=1}^{2}\frac{Z}{R_{ij}}+\frac{\gamma^2}{2}(x_i^2+y_i^2)\right]+\gamma\ (L_z+2S_z)+\frac{1}{r_{12}}+\frac{Z^2}{R}\ , \qquad (2)$$

where $L_z=\ell_{1z}+\ell_{2z}$ and $S_z=s_{1z}+s_{2z}$ are the z component of the total angular momentum and spin of the system, respectively, and lengths are in units of the Bohr radius a_0.

Eigenstates of the above Hamiltonian can be written as a product of a coordinate and a spin function (or a linear combination of such products), $\Psi(\mathscr{R},\Sigma) = \Phi(\mathscr{R}) \otimes \chi(\Sigma)$, because $[\hat{\mathscr{H}},S^2]=0$ $[\mathscr{R}=(\mathbf{r}_1,\mathbf{r}_2)$, $\Sigma=(s_1,s_2)]$. The eigenvalues of S^2,S_z, and parity Π ($\Pi|\mathscr{R}\rangle=|-\mathscr{R}\rangle$) are good quantum numbers. Since we will only consider the classically stable (minimum-energy) configuration, that is, the one where magnetic field direction (z) and internuclear axis coincide, one can also classify the electronic states according to the eigenvalues of L_z.

It is important to stress that, for a nonzero field, this constant of motion appears as a consequence of the (symmetric) gauge adopted. For an arbitrary gauge $\mathbf{A}$ we should consider as symmetry the z component of the gauge-covariant operator $\tilde{\mathbf{L}}=\Sigma_i\mathbf{r}_i\wedge[\boldsymbol{\Pi}_i-(e/c)\mathbf{A}_s]$. The Cartesian components of this operator satisfy the algebra of angular momentum $[\tilde{L}_\mu,\tilde{L}_\nu]=i\hbar\epsilon_{\mu\nu\lambda}\tilde{L}_\lambda$ with Casimir operator $\tilde{\mathbf{L}}^2([\tilde{L}_\mu,\tilde{\mathbf{L}}^2]=0)$. Notice, however, that $L_z\Phi=M\Phi$ implies $\tilde{L}_z\tilde{\Phi}=M\tilde{\Phi}$, with $\tilde{\Phi}=\exp[-i\Lambda]\Phi$, where the gauge function Λ satisfies $\mathbf{A}=\mathbf{A}_s+\nabla\Lambda$. That means that the states are labeled with the same quantum numbers; it is only their meaning that is gauge dependent.

For the superstrong range of field strength, the sector of $S=0$ is irrelevant for the low-energy spectrum, and only the completely spin-polarized one, $S=1$, will be analyzed. Then, the configurational part of the wave function $\Phi(\mathscr{R})$ is antisymmetric. In the following we will determine, using stochastic techniques, the sector of L_z (or $\tilde{L}_z$) to which the ground state Φ_0 belongs.

The basic difficulty in solving the stationary Schrödinger equation $\hat{\mathscr{H}}\Phi=E\Phi$ for arbitrary magnetic field strength lies in the different symmetries furnished by the Coulomb and Lorentz forces, which prevent closed-form analytic solutions. In order to study the spectrum of $\hat{\mathscr{H}}$ we rely on projector methods that are based on the property that for large imaginary times (τ), the Euclidean evolution operator acting on a parent state Φ_T (of a given symmetry) projects out the state Φ_0: $\Phi_0 \propto \lim_{\tau\to\infty}\exp[-\tau(\hat{\mathscr{H}}-E_T)]\Phi_T$, which is the lowest-energy state with a component in Φ_T ($\langle\Phi_0|\Phi_T\rangle\neq 0$), where E_T is a suitable trial energy that shifts the zero of the energy spectrum. To generate the stochastic process that yields the asymptotics, we need a probability measure (real and positive definite function) to sample points in configuration space. The difficulty caused by Fermi antisymmetry and the fact that $\hat{\mathscr{H}}$ is a complex Hermitian operator arise from an instability in the process that is reflected in the variance of the computed expectation values. To overcome this problem we have recently developed [6] a quantum Monte Carlo approach to deal with physical systems whose many-particle wave functions (or density matrices for finite temperatures) are necessarily complex (e.g., fermions in an external magnetic field). We reformulate the nonrelativistic quantum mechanics in terms of the modulus $|\Phi|$ and phase φ of the scalar N-particle state $\Phi(\mathscr{R})=|\Phi(\mathscr{R})|\exp[i\varphi(\mathscr{R})]$, where $\mathscr{R}=(\mathbf{r}_1,\ldots,\mathbf{r}_i,\ldots,\mathbf{r}_N)$ denotes a point in configuration space (a Cartesian manifold of dimension d N, where d is the spatial dimension). Then, the stationary Schrödinger equation is equivalent to solving two real (coupled) differential equations for $|\Phi|$ and φ, which in the present context reads

$$\hat{H}|\Phi(\mathscr{R})|=\left[\hat{\mathscr{H}}_{M,M_S}+\sum_{i=1}^{N}\frac{\mathscr{A}_i^2}{2}\right]|\Phi(\mathscr{R})|=E|\Phi(\mathscr{R})|, \tag{3}$$

$$\sum_{i=1}^{N}\nabla_i\cdot[|\Phi(\mathscr{R})|^2\mathscr{A}_i(\mathscr{R})]=0\ , \tag{4}$$

where $\mathscr{A}_i=\nabla_i\varphi$ and $\hat{\mathscr{H}}_{M,M_S}$ is the Hamiltonian of Eq. (2) already projected onto the subspace with quantum numbers M and M_S, i.e., $L_z\Phi=M\Phi$ and $S_z\Phi=M_S\Phi$. The essence of the *fixed-phase* (FP) method consists in making a choice for φ and solving *exactly* the bosonic problem for $|\Phi|$ [Eq. (3)], using stochastic techniques (e.g., Green's-function Monte Carlo).

The question that naturally arises is how the phase functions φ are chosen. There are some mathematical constraints that the phases ought to satisfy. They should, for example, conserve the symmetries of the Hamiltonian (unless some are spontaneously broken) and particle statistics. It can be easily proved that the method provides a variational upper bound for the energy and, for a prescribed trial phase φ_T, the *lowest* energy consistent with this phase. A phase that satisfies Eq. (4) (*continuity equation*) will lead to the *exact* solution of this many-fermion problem. Once a trial phase has been chosen, to solve the eigenvalue equation (3) within each subspace (M,M_S), we transform the time-dependent Schrödinger equation for $|\Phi|$ in Euclidean time τ to a master equation for the *importance-sampled* distribution $P(\mathscr{R},\tau) = |\Phi_T(\mathscr{R})|\,|\Phi(\mathscr{R},\tau)|$ $(N=2)$,

$$\frac{\partial P(\mathscr{R},\tau)}{\partial\tau}=\sum_{i=1}^{2}\nabla_i\cdot[\tfrac{1}{2}\nabla_i P(\mathscr{R},\tau)-\mathbf{F}_i(\mathscr{R})\,P(\mathscr{R},\tau)] -(E_L(\mathscr{R})-E_T)P(\mathscr{R},\tau)\ , \tag{5}$$

and use stochastic random walks in configuration space $[\mathscr{R}=(\mathbf{r}_1,\mathbf{r}_2)]$ to solve this equation. $\mathbf{F}_i(\mathscr{R})=\nabla_i\ln|\Phi_T|$ is the *drift velocity* whose role is to guide the random walk towards regions of phase space where the trial function is larger, and $E_L(\mathscr{R})=|\Phi_T|^{-1}\hat{H}|\Phi_T|$ is the local energy.

The phase $\varphi_T(M,M_S)=-i\ln[\Phi_T/|\Phi_T|]$ is chosen from the trial function

$$\Phi_T(\mathscr{R})=\exp\left[\frac{r_{12}}{4+\sqrt{a_1\rho_{12}^2+a_2z_{12}^2}}-\sum_{i,j}\frac{ZR_{ij}}{1+b\ R_{ij}}\right] \times[g_+(\mathbf{r}_1)g_-(\mathbf{r}_2)-g_+(\mathbf{r}_2)g_-(\mathbf{r}_1)] \tag{6}$$

whose modulus is used as an importance function to *guide* the random walk. In Eq. (6),

$$g_\pm(\rho,\phi,z)=\rho^{|m_\pm|}\exp[im_\pm\phi-F_\pm(\rho,z)]\ , \tag{7}$$

with

$$F_{\pm}=\mu\rho^2+\frac{\kappa_{\pm}|z\pm\tilde{R}|^2}{1+\alpha_{\pm}|z\pm\tilde{R}|}-\ln(\nu_1+|z\pm\tilde{R}|^{\nu_2}) \quad , \qquad (8)$$

where $a_i, b, \mu, \kappa_{\pm}, \alpha_{\pm}, \tilde{R}, \nu_i$ are variational parameters. The full trial function, in addition to having the antisymmetric product of one-body states $g_{\pm}$, also has a Jastrow factor with electron-electron and electron-nuclear two-body correlation functions that satisfy Kato cusp conditions at the collision points. It is straightforward to prove that Φ_T is an eigenstate of L_z with eigenvalue $M=m_+ + m_-$ and, for $\tilde{R}=0$, it is a state of parity $(-1)^M$ (or z-parity $+1$). At sufficiently long times, the steady-state distribution $P(\mathscr{R},\tau\to\infty)\to|\Phi_T(\mathscr{R})|\ |\Phi_{M,M_S}(\mathscr{R})|$ (up to a normalization constant), where Φ_{M,M_S} is the lowest-energy state, compatible with the phase $\varphi_T(M,M_S)$, which has a component in Φ_T. In order to get this stationary distribution, E_T must be adjusted to be equal to the lowest subspace energy E_{M,M_S}, given in turn by $E_{M,M_S}=\lim_{\tau\to\infty}\langle E_L(\mathscr{R})\rangle_{P(\mathscr{R},\tau)}$. As long as Φ_T satisfies the right symmetries, the functional form of its modulus affects *only* the convergence and statistical fluctuations of E_{M,M_S}.

We start our calculations at the variational Monte Carlo (VMC) level in the variance minimization version [7]. To this end we vary the free parameters in Φ_T in order to minimize the fluctuations in the local energy $\sigma^2=\int d\mathscr{R}|\Phi_T|^2[E_L(\mathscr{R})-E_T]^2/\int d\mathscr{R}|\Phi_T|^2$. This strategy provides a balanced optimization of the wave function and has a known lower bound (namely zero). Once the trial wave function has been optimized we use the walkers generated with a multiparticle Metropolis algorithm to compute the expectation value of the observables of interest, which for our present purposes consists only of the total energy spectrum $E_{M,M_S}=\langle\Phi_T|\hat{\mathscr{H}}\Phi_T\rangle/\langle\Phi_T|\Phi_T\rangle$.

The results of this calculation ($Z=1$) are depicted in Fig. 1 for two different values of magnetic field strength. In this figure we show the total energies as a function of the internuclear separation R for two different symmetry states, namely $(M,M_S)=(0,0)$ and $(-1,-1)$. The energy of the state (0,0) decreases monotonically as a function of increasing R, reaching asymptotically the limit of two isolated H atoms in the $1s$ state. Because of statistical uncertainty it is not possible to determine whether a shallow minimum develops in this curve. On the other hand, the state $(-1,-1)$, which is the ground state in this superstrong regime, presents a deep minimum at the equilibrium nuclear separation R_e, with a limiting energy value that corresponds to having one H atom in the $1s$ and another in the $2p_{-1}$ states. In the $R\to\infty$ limit, our trial wave function yields the *exact* energies [3] within the statistical error bar. However, for the largest magnetic fields considered, some correlation energy is missing in $E_{(-1,-1)}(\infty)$. This small energy difference is restored with our FP method, which in the above mentioned limit is essentially exact because the nodal surface structure of the many-fermion wave function is irrelevant.

To determine the bonding parameters we have fitted the VMC data to the modified Morse potential of Hulburt and Hirschfelder [8] and used this function (and not the Hellman-Feynman theorem $\langle\Phi_T|\partial_R\hat{\mathscr{H}}\Phi_T\rangle = 0$) to compute them.

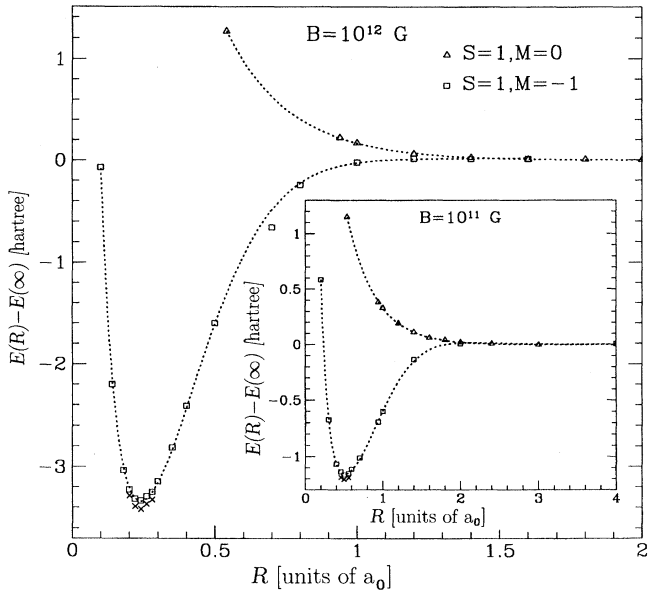

FIG. 1. The VMC total energy of H_2 as a function of the internuclear separation R for the (0,0) and $(-1,-1)$ states. The symbols correspond to the Monte Carlo calculations while the dotted lines are the result of a fit to a modified Morse potential. The energies are defined with respect to their values in the infinite separation limit, which are $E_{(0,0)}(\infty)=-11.925(4)$ and $E_{(-1,-1)}(\infty)=-10.234(11)$ in Hartree atomic units. These can be compared to the *exact* [3] atomic values (after interpolation) -11.9206 and -10.2603, respectively. For comparison, we also show the FP energy results (crosses) around the equilibrium configuration. The inset corresponds to a different magnetic field strength. In this case, $E_{(0,0)}(\infty)=-5.7197(21)$ and $E_{(-1,-1)}(\infty)=-4.794(4)$, while the *exact* atomic values are -5.7185 and -4.7984, respectively.

Table I displays these results. As a function of increasing field strength, the molecule gets smaller and the dissociation energy increases, which suggests that a low-density gas of H atoms under such conditions has a tendency to form a strong bonded molecular phase and not a superfluid one as has been proposed [2,1].

In order to go beyond the VMC results we start our FP computation assuming the phase φ_{M,M_S} within each subspace. We begin at $\tau=0$ with an ensemble of $N_c=200$ configurations $\mathscr{R}_i$ $(i=1,\ldots,N_c)$ distributed according to $P(\mathscr{R})=|\Phi_T|^2$, then diffuse and drift each configuration as $\mathscr{R}_i'=\mathscr{R}_i+\tau\,\mathbf{F}(\mathscr{R}_i)+\eta$, where η is a normally distributed random variable with a variance of τ, and branch with the local energy. The total number of configurations is then relaxed by propagation in imaginary time and stabilized when it approximates the stationary distribution

TABLE I. Interatomic equilibrium separation R_e (in units of a_0), vibrational frequency ω_e (in units of 10^4 cm^{-1}), and total ground-state energy $E_{(-1,-1)}$ (in eV) for the H_2 molecule.

B (10^{12} G)	R_e	ω_e	$-E^{VMC}_{(-1,-1)}$	$-E^{FP}_{(-1,-1)}$	$-E_{(-1,-1)}$ [9]
0.1	0.51	2.37(1)	162.4(1)	163.03(5)	160.3
1.0	0.24	8.26(4)	369.9(3)	372.4(2)	368.6

$P(\mathscr{R}, \tau \to \infty) \to |\Phi_T(\mathscr{R})|\ |\Phi_{M,M_S}(\mathscr{R})|$. In Table I we present the FP ground-state results at the equilibrium nuclear configuration R_e, and compare them to the Hartree-Fock calculations of Lai *et al.* [9]. We find about 2% lower energy. For the subspace (0, 0), in the range of magnetic field strengths considered, the FP approach does not correct the VMC energy values within the statistical uncertainty, reflecting the high quality of the trial wave function used.

Finally, let us summarize our analysis of the ground-state symmetry as a function of increasing magnetic field strength. In the weak field regime ($\gamma \leqslant 10^{-3}$), the ground state belongs to the subspace (0, 0) $^1\Sigma_0$, while in the superstrong regime ($3\times10^3 > \gamma \gg 1$) it belongs to $(-1,-1)$ $^3\Pi_0$. This non-time-reversal invariant state has a strong interatomic interaction, suggesting that a hydrogen gas will form a strong bonded molecular phase and not a Bose-Einstein condensate as has been suggested in Ref. [2], whose conclusion was based on the wrong symmetry state [namely (0, 0) $^3\Sigma_0$]. The singlet-triplet transition takes place in the intermediate field regime ($\gamma \approx 0.3$), as indicated in Fig. 2. It seems instructive to point out that a similar symmetry transition happens in a He atom [10]. This is not surprising since a He atom is a H_2 molecule with zero internuclear separation. Other triplet-triplet ground-state transitions could take place for even stronger field strengths ($\gamma \gg 3\times10^3$), involving larger values of $|M|$. Again, this could happen as a result of the competition between rotational and Coulomb energies: as the field gets larger the system tends to shrink and, to minimize the Coulomb interaction, it tends to raise the angular momentum, increasing in this way the average distance between electrons. Notice that, in this regime of magnetic fields, the electrons become relativistic. M-symmetry phase transitions have been predicted, in a different context, for quantum dot He [11].

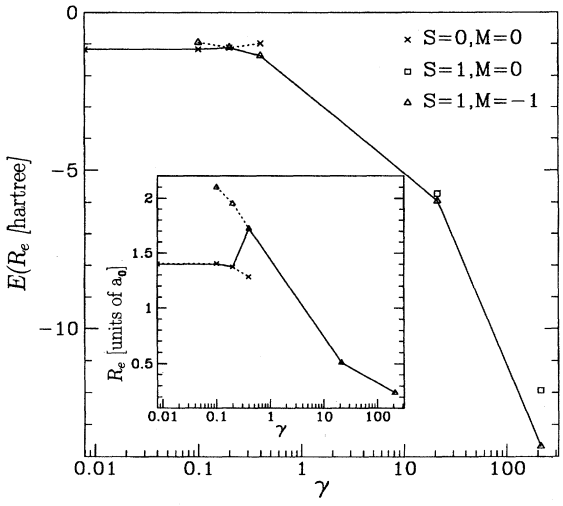

FIG. 2. Structural ground-state properties of H_2 as a function of magnetic field strength. $E(R_e)$ is the total energy at the equilibrium internuclear separation R_e. Notice that R_e increases at the singlet-triplet transition. Because of the repulsive nature of the state (0,0) $^3\Sigma_0$, the squares represent its energy value for $R \to \infty$. The lines are just a guide to the eye.

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