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Hartree-Fock study of molecules in very intense magnetic fields

M. Demeur and P.-H. Heenen
Physique Nucléaire Théorique, Université Libre de Bruxelles, Code Postal 229, 50 avenue F. Roosevelt, B-1050, Brussels, Belgium

M. Godefroid
Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, Code Postal 160/09, 50 avenue F. Roosevelt, B-1050, Brussels, Belgium

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We investigate the stability of homonuclear diatomic molecules from H_2 up to C_2 and of the finite chains H_n $(n \leq 5)$ and He_n $(n \leq 4)$ immersed in very intense magnetic fields ($B \approx 10^8$ T). The atomic and molecular total energies are calculated within the one-dimensional Hartree-Fock approximation, using a Lagrange basis set associated with a Cartesian mesh. The stability of the molecules decreases beyond Li_2 although all the studied molecules are found stable. The energy per atom of H and He finite chains stabilizes already for the small chain sizes that we have investigated.

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I. INTRODUCTION

The discovery of pulsars and their interpretation as neutron stars has renewed the interest of physicists in the study of matter immersed in very intense magnetic fields ($B \approx 10^8$ T). In particular, the possibility that atoms could form chains of infinite polymers has been the subject of many investigations [1,2]. Since the beginning of the 1970's the hypothesis of the existence of infinite linear polymers of iron at the neutron star surfaces has prevailed. However, a more recent calculation of Neuhauser, Koonin, and Langanke [2] has contradicted this hypothesis.

The electronic structure of *atoms* and one-dimensional *infinite chains* in strong magnetic fields has been investigated through variational methods [3–5], Thomas-Fermi [6], Hartree-Fock [2,7–9], and density-functional calculations [10,11]. Very little attention, however, has been paid to the study of light *molecules*. Apart from its intrinsic interest, such a study can shed light on the results of Neuhauser, Koonin, and Langanke [2].

The first physicists who considered the molecular behavior in very intense magnetic fields were Kadomtsev and Kudryavtsev [12]. Unfortunately, their calculations suffer from various troubles: erroneous kinetic energy and too vigorous numerical approximations. The total energies they obtained are lower than the exact ones, contradicting the variational theorem. A similar situation occurs in the paper by Constantinescu and Rehak [13]. Besides these two studies, an interesting conjecture has been made by Ruderman [1] concerning the structure of H_n molecules. More recently, Lai, Salpeter, and Shapiro [9] have studied the electronic structures of hydrogen polymolecules H_n $(n \leq 4)$ and infinite chains.

The electrons of the atoms or the molecules are antialigned along the very strong magnetic-field direction: their behavior is the one of a collection of spinless fermions. Their total wave function is basically a completely antisymmetric spatial function of the individual variables. In order to build the ground state of an atom, the individual wave functions have to be chosen among the lowest Landau states, their degeneracy being removed by the Coulomb interaction with the nuclei. The growth of the individual energies is monotonic as a function of the projection of the angular momentum along the field direction. As shown by Rau, Mueller, and Spruch [14], some atomic shell structure could appear in the so-called "strong" field regime (in contrast with the "ultrastrong" fields) in which the magnetic field is not large enough to keep all electrons in the deep levels characterized by nodeless longitudinal wave functions. For a given magnetic field, the higher the nuclear charge, the more the appearance of nodes is expected. As explicitly illustrated by the calculations of Neuhauser, Koonin, and Langanke [2], no shell structure appears at $B_{12}=1-5$, even for an atom as heavy as iron ($Z=26$). The lack of periodicity arising from the nonexistence of shell structure will lead to a very poor chemistry, which is opposite of our terrestrial environment. More specifically, atomic systems immersed in a 10^8 T field will never produce an inert gas family. Molecules such as He_2 and HeH will be as bound as any other diatomic molecule of very light elements.

In order to evaluate the binding energies of light molecules in strong magnetic fields, one of us [15] proposed some years ago the use of a basis—called spheröidal—composed of the well-known one- and two-dimensional harmonic-oscillator functions for longitudinal and transverse motions. Such a choice simplifies the calculation of matrix elements although Gaussian functions are not well adapted to the asymptotic behavior of molecular states. These functions were used by Demeur and Mowlavi [16] who calculated the total and dissociation energies of H_2 and H_3. The same basis was used by Kabbadj [17] in order to evaluate the binding energy of HeH. However, such individual wave functions lead to cumbersome optimizations, the variational parameters appearing in nonlinear expressions. Moreover, they are not very well adapted to the description of molecular states, which require the use of a different basis for each center. It was concluded that this approach was not suitable for the study of systems involving an increasing number of electrons and nuclei. Therefore, we moved to the Hartree-Fock method on a one-dimensional cartesian mesh in which the discretization approach on a basis of Lagrange functions associated with the mesh [18] has many advantages over common variational basis-set calculations. Like the numerical methods adopted by Virtamo [7] or Pröschel *et al.* [8] for atoms or by Lai, Salpeter, and Shapiro [9] for molecules, no prior assumption about the form of the longitudinal wave functions has to be made, as required in basis-set calculations [19]. It provides in a straightforward way an approximation of the longitudinal wave-function amplitudes based on their values at the mesh points and the variational parameter is limited to a scaling factor which determines the box extension along the magnetic field.

The "Hartree-Fock method on a mesh" is described in Sec. II, with a discussion of the achieved accuracy and convergence of the energies. In Sec. III, we focus on the results obtained for homonuclear diatomic molecules and finite chains and on their interpretation in terms of molecular stability.

II. HARTREE-FOCK CALCULATIONS

The total Hamiltonian of a system of electrons and nuclei in a uniform magnetic field can be written as the sum of four terms:

$$H=\sum_{i} h_i^B+\sum_{i,\alpha} V_{i\alpha}+\sum_{\substack{i,j\\ i<j}} V_{ij}+\sum_{\substack{\alpha,\beta\\ \alpha<\beta}} V_{\alpha\beta} \ . \tag{1}$$

h_i^B is the Hamiltonian of electron i in the homogeneous and constant magnetic field B, and the three potential terms represent the Coulomb interaction between the electrons and nuclei, labeled by latin and greek letters, respectively. If the magnetic field is chosen parallel to the z axis, the magnetic Hamiltonian h_i^B can be written as

$$h_i^B=h_{\perp i}^B+T_{zi} \ , \tag{2}$$

where $h_{\perp i}^B$ is the transverse magnetic Hamiltonian of electron i and T_{zi} is its longitudinal (or parallel) kinetic energy. In the Born-Oppenheimer approximation, the nuclear repulsion energy

$$\sum_{\alpha<\beta} V_{\alpha\beta}=\sum_{\alpha<\beta}\frac{Z_\alpha Z_\beta e^2}{|\mathbf{r}_\alpha-\mathbf{r}_\beta|} \tag{3}$$

is merely an additive contribution to the total energy.

We are interested in a Landau regime where the magnetic field is dominant and is only slightly perturbed by the Coulomb interactions. It is strong enough to align the electron spins. The total wave function Ψ can then be approximated by a Slater determinant built on the n spatial one-electron functions $\{\psi_i;\, i=1,n\}$, multiplied by the symmetric product of the antiparallel spin functions.

We assume that the motion perpendicular to the magnetic field is described by the lowest-order Landau functions, corresponding to the lowest radial quantum number $n=0$ and $\Lambda\leq 0$,

$$\phi_{n=0,\Lambda}(\rho,\varphi;b_\perp)=\left[\frac{1}{\pi\lambda! b_\perp^2}\right]^{1/2} e^{-i\lambda\varphi} e^{-(\rho^2/2b_\perp^2)}\left[\frac{\rho}{b_\perp}\right]^{\lambda} , \tag{4}$$

where $\lambda\equiv|\Lambda|$.

Introducing the dimensionless field-strength parameter $\gamma=B\hbar^3/m^2ce^3$, as a measure of the relative strengths of the magnetic and Coulomb fields, we will consider very intense magnetic fields corresponding to $\gamma=1000$. In these extreme conditions, the transverse parameter $b_\perp$ is fixed to the Larmor radius b_0 for the transverse functions

$$b_\perp\equiv b_0=\left[\frac{\hbar}{m\omega_0}\right]^{1/2}=\left[\frac{2\hbar c}{eB}\right]^{1/2} \tag{5}$$

and each wave function can be factorized as

$$\psi_i(\mathbf{r})=\phi_{0,\Lambda_i}(\rho,\varphi;b_0)\chi_{n\parallel_i}^{\Lambda_i}(z) \ . \tag{6}$$

In this scheme, the Coulomb interaction only affects the longitudinal wave functions $\chi_i(z)$ and the motion perpendicular to the magnetic field is described by unperturbed Landau states.

Using the factorization (6), assuming the orthonormality of the individual wave functions $\langle\psi_i|\psi_j\rangle=\delta_{ij}$ and averaging the motion in the transverse plane (i.e., integrating over the variables ρ and φ), one gets the following total-energy expression (in Ry units):

$$\begin{aligned}\langle\Psi|H|\Psi\rangle=&\sum_{\alpha<\beta}\frac{Z_\alpha Z_\beta}{|\mathbf{r}_\alpha-\mathbf{r}_\beta|}+\sum_i\langle\chi_i(z)|-\frac{d^2}{dz^2}-\sum_\alpha V^{\lambda_i}(|z-z_\alpha|)|\chi_i(z)\rangle\\ &+\sum_{i<j}\sum_k[f^k(ij)\langle\chi_i(z_1)\chi_j(z_2)|v^k(|z_1-z_2|)|\chi_i(z_1)\chi_j(z_2)\rangle\\ &-g^k(ij)\langle\chi_i(z_1)\chi_j(z_2)|v^k(|z_1-z_2|)|\chi_j(z_1)\chi_i(z_2)\rangle] ,\end{aligned} \tag{7}$$

where

$$V^\lambda(|z-z_\alpha|)=\left[\frac{\gamma}{2}\right]^{1/2}\frac{1}{\lambda!}\int_0^\infty\frac{w^\lambda e^{-w}}{\left[w+\frac{\gamma}{2}(z-z_\alpha)^2\right]^{1/2}}dw \ . \tag{8}$$

The expression for $v^k(|z_1-z_2|)$ is obtained by replacing in (8) γ by $\gamma/2$. The coefficients $f^k(ij)$ and $g^k(ij)$ result from the integration of the electrostatic operator between the Landau functions in the transverse plane. This step involves the use of the orthogonal transformation between the eigenfunctions of the two-electron Hamiltonian

$H=h_1+h_2$ where h_i is the Hamiltonian of electron i in a two-dimensional harmonic potential, into those of the harmonic-oscillator Hamiltonian $H=h_{\text{rel}}+h_{\text{c.m.}}$ expressed in the relative and center-of-mass variable, respectively [15].

Applying the variational principle to the expression (7) with respect to any variation $\delta_{\chi_i}(z)$ yields the one-dimensional Hartree-Fock equations for the longitudinal wave functions in the direction parallel to the magnetic field. We have chosen to describe the individual wave functions by a discretization on a one-dimensional Cartesian mesh, composed of equidistant points. This limits the number of parameters of the calculation to two: the mesh size h and the number of mesh points N (or equivalently, the distance $Nh/2$ from the origin beyond which the wave functions are set equal to zero). It has been shown [18] that such a discretization is equivalent to an expansion on a basis composed of Lagrange functions $f_p(z)$,

$$\chi_i(z)=\sum_{p=1}^{N}\chi_i(z_p)f_p(z) , \tag{9}$$

where $\chi_i(z_p)$ are the values of the χ's at the mesh points z_p. The functions $f_p(z)$ have very special properties,

$$f_p(z_q)=\delta_{pq} , \tag{10}$$

$$\int_{-N/2}^{N/2} f_p^*(z)f_q(z)dz=\delta_{pq} , \tag{11}$$

and their analytical form is given by

$$f_p(z)=\frac{1}{N}\frac{\sin\pi(z-p)}{\sin[\pi(z-p)/N]} \tag{12}$$

using the mesh size as unit of length.

The Hartree-Fock equation projected on the Cartesian mesh $\{|p\rangle\equiv f_p(z);p=1,\ldots,N\}$ has the following form for the longitudinal wave function $\chi_i(z)$:

$$\sum_r\left\{T_{\text{pr}}-\sum_\kappa\langle p|V^{\lambda_i}(|z-z_\kappa|)|r\rangle+\sum_{\substack{i,j\\ j\neq i}}\sum_k\sum_{qs}\chi_j(z_q)\chi_j(z_s)[f^k(ij)\langle pq|v^k|rs\rangle-g^k(ij)\langle pq|v^k|sr\rangle]-\epsilon_r^i\delta_{\text{pr}}\right\}\chi_i(z_r)=0 . \tag{13}$$

Orbitals belonging to the same Λ subspace are orthogonalized longitudinally in the variational procedure without affecting the variational content of the total wave function.

Using the analytical form (12), the Laplacian of $f_p(z)$ can be calculated exactly. In [18], the one-dimensional kinetic-energy integrals T_{pr} have been computed by use of the Gauss formula associated with the Cartesian mesh which turns out to be exact for this matrix element. Thanks to this formula, the only values of the χ entering the calculation are the values at the mesh points. In a study of two-electron atoms [20] using a mesh built on Laguerre polynomials, it has been shown that the accuracy of a Gauss quadrature formula limited to the mesh points is not sufficient for a problem involving the Coulomb interaction. We therefore chose to compute the integrals of the electron-proton and electron-electron interactions with a Gauss formula associated with a Cartesian mesh denser than the discretization describing the individual wave functions. The one-body integrals

$$\langle p|V^{\lambda_i}(|z-z_\kappa|)|r\rangle\equiv\langle f_p(z)|V^{\lambda_i}(|z-z_\kappa|)|f_r(z)\rangle \tag{14}$$

were evaluated with n_1 points, while the two-body integrals

$$\langle pq|v^k(|z_1-z_2|)|rs\rangle$$
$$\equiv\langle f_p(z_1)f_q(z_2)|v^k(|z_1-z_2|)|f_r(z_1)f_s(z_2)\rangle , \tag{15}$$

which are minor contributions to the mean field, were computed with n_2 points ($N<n_2<n_1$).

We wrote a computer program, based on this "Hartree-Fock-on-a-mesh" method, for the study of linear chains of atoms. The length of the chain is *a priori* arbitrary, but of course finite. No restrictions are imposed on the charge of the nuclei composing the chains, making possible the study of chains built with either identical or different atoms, including the atomic case.

Results of convergence tests on the hydrogen atom ground-state energy are shown in Table I for $\gamma=1000$ as a function of the number N of Lagrange functions and n_1 of integration points of the potential. The energies reported in this table correspond to the optimal mesh size h_{opt}.

The comparison of energies corresponding to similar integration meshes (n_1) gives a measure of the quality of the Lagrange basis associated with the N-point Cartesian mesh. For a given N, the variation of the energy with n_1 reflects the accuracy of the Gauss quadrature integration of the potential. For $N=16$, a few hundred points are required to achieve an accuracy better than 10^{-3} while the use of a number of integration points equal to the number of discretization points leads to a large inaccuracy. One can see that a very good convergence can be achieved with still a reasonable number of integration points.

The total energies of the low-lying Landau states ($\lambda=0,1,\ldots,5$) of hydrogen are reported in Table II for $N=16$ and $n_1=304$ and compared with the adiabatic values of Friedrich [21]. The results turn to be accurate with this rather small Lagrange basis set.

The h_{opt} trend illustrates the role of the mesh size in our calculations. It defines a box extension and its optimal value corresponds to the best distribution of the

TABLE I. Total energies (E in Rydbergs) of the ground state of hydrogen ($\lambda=0$), using a Cartesian mesh built on N Lagrange functions and integrating the one-body terms with n_1 points. The field strength γ is equal to 100 and h_{opt} is the optimal mesh size.

λ	N	n_1	E	h_{opt}
0	16	16	−11.555	0.13
		304	−15.160	0.13
		528	−15.173	0.13
		1520	−15.177	0.13
	20	380	−15.206	0.11
	40	440	−15.255	0.07
	160	480	−15.264	0.018
	500	500	−15.265	0.006
		1500	−15.278	0.007
		2500	−15.280	0.007

Lagrange functions avoiding significant distortion of the wave function near the singularities (i.e., the nuclei positions) and beyond the last point of the mesh on both sides of the atom or molecule. In this respect, it decreases with increasing N for the same state (see Table I). On the other hand, the description of more extended wave functions corresponding to higher-lying states with increasing λ requires larger mesh sizes for the same number of functions ($N=16$).

The atomic ground states of H, He, Li, Be, B and C, have been calculated using a $N=16$ Cartesian mesh and a Gauss quadrature integration with n_1 points for the one-body term and n_2 for the two-body term. We have taken $n_1=528$ for $Z\leq 4$, $n_1=880$ for $Z\geq 5$, and $n_2=176$ for all Z's. This choice has been governed by a compromise between the N^4 scaling law in the number of two-electron integrals, the N^2 size of the Hartree-Fock eigenvalue problem, the Lagrange basis set quality, and the numerical integration accuracy. Our $\gamma=1000$ results are presented in Table III, with the numerical results of Neuhauser, Koonin, and Langanke [2] for $\gamma=425.53$ and 2127.66. For these two field strength values, our H and He results (not reported in the table) are 161 and 573 eV ($\gamma=425.53$) and 255 and 950 eV ($\gamma=2127.66$) in very good agreement (better than 1%) with Neuhauser, Koonin, and Langanke [2] results and with previous He calculations [7,8].

III. RESULTS AND DISCUSSION

In addition to the atomic states considered in Tables I–III, a variety of excited atomic states had to be considered in order to determine the most favorable partitions resulting from the molecular dissociation. Among all these results, we only present those essential for the evaluation of the dissociation energy of the molecular states we are interested in. All results reported in this chapter have been calculated at $\gamma=1000$ (i.e., $B=2.35\times 10^{12}$ G).

A. Diatomic molecules

Results concerning the lowest configurations of diatomic homonuclear molecules from H_2 to C_2 are summarized in Table IV. The configurations are characterized by the λ sequence of the electrons and are denoted $[(\lambda_1)_{\nu_1}\cdots(\lambda_n)_{\nu_n}]$ where ν gives the number of the orbitals having a specific value of λ ($\nu\equiv 1$ is omitted).

The ground states of H_2, He_2, and Li_2 correspond to configurations in which all the electrons have different values of λ. Thanks to the growing nuclear attraction, the situation changes gradually for heavier molecules. The first excited orbitals corresponding to the lower λ values become energetically more favorable than the unexcited orbitals with larger λ's. In Li_2, the

TABLE II. Total energies (E in Rydbergs) at $\gamma=1000$ of some low-lying states ($\lambda=0,1,\ldots,5$) of the hydrogen atom, using a Cartesian mesh built on $N=16$ Lagrange functions and integrating the one-body terms with $n_1=304$ points; h_{opt} is the optimal mesh size.

λ	N	n_1	E	h_{opt}	Other[a]
0	16	304	−15.160	0.13	−15.280
1	16	304	−11.221	0.16	−11.266
2	16	304	−9.571	0.17	
3	16	304	−8.585	0.18	
4	16	304	−7.903	0.19	
5	16	304	−7.391	0.20	

[a] Friedrich [21].

TABLE III. Absolute values of the ground-state total energies (eV) of atoms for different field strengths. The ($\gamma=1000$) values have been calculated using $N=16$ Lagrange functions with an ($n_1=528-880/n_2=176$) integration mesh. The two other sets of results are taken from Neuhauser, Koonin, and Langanke [2].

		NKL[a]	This work	NKL[a]
$B(10^{12}$ G)		1	2.35	5
γ		425.53	1000	2127.66
H	[0]	161	206	255
He	[0–1]	574	754	958
Li	[0–2]	1209	1611	2076
Be	[0–3]	2042	2746	3584
B	[0–4]	3054	4139	5456
C	[0–5]	4200	5773	7600

[a] Neuhauser, Koonin, and Langanke [2].

configuration $[0_2 1234]$ lies only a few Rydbergs higher than the ground configuration [012345], with an equilibrium internuclear distance appreciably larger ($r=0.26a_0$). From Be_2, the configuration with two $\lambda=0$ electrons is definitely more favorable energetically than the configuration with all different λ's. When increasing the nuclear charge, the first excited orbitals $\lambda=1$ and 2 become also competitive and are occupied in the ground configuration of B_2. In C_2, the $\lambda=0$, 1, 2, 3 and 4 first excited orbitals are all occupied. This evolution is most likely the key to the molecular problem in strong magnetic fields.

A parallel change can be observed in the nuclear equilibrium interdistances. For H_2, He_2, and Li_2, these are close to the longitudinal value of $\sqrt{\langle z^2 \rangle}$ relative to atomic states at the same value of γ. For Be_2, the internuclear distance is appreciably larger. Due to the growing nuclear attraction, the two $\lambda=0$ electrons become more tightly bound, screening the two nuclei against the other electrons. If this screening was complete, Be_2 $[0_2 123456]$ could be approximated as the excited configuration $[12\ldots6]$ of Li_2, with a nuclear interdistance larger than the Li_2 $[01\ldots5]$ ground state. This effect is even amplified for B_2 and C_2. In the latter case, the two Hartree-Fock $\lambda=0$ orbitals have very close individual energies and their wave functions are mainly localized on a different nucleus, having a very high atomic character. This localization is due to two factors. First, the Coulomb repulsion between the nuclei increases as Z^2 and moves the nuclei apart, enhancing the atomic character of the lower orbitals. The second factor is related to the narrowing of the electronic wave functions for the atoms when Z increases. The wave functions of the excited states indeed behave like the wave functions of the field-free one-dimensional hydrogenic ion and consequently scale as Z^{-1}. The wave functions of the lowest $\lambda=0$ state of the atoms have a longitudinal extension considerably lower than all the excited states. We have verified that this narrowing is enhanced when Z is increased.

The dissociation of the molecules in two atoms can lead to partitions differing by the λ's of the electrons. The energetically most favorable partitions are given in Table IV, together with the corresponding dissociation energies. Once more H_2, He_2, and Li_2 behave similarly but differently from Be_2, B_2, and C_2. The fact that couples of electronic wave functions have the same value of λ leads to less excited atoms as dissociation products, giving rise to a faster lowering of the dissociation limit (E_A+E_B). As a result, the dissociation energy E_D increases from H_2 to Li_2 but begins to decrease at Be_2. The stability evolution is illustrated in Fig. 1 in which we plotted, for each molecule, the dissociation energies of both, the most favorable configuration and the configuration containing only different values of λ. The dissociation energy increases monotonically for the latter, while it starts to decrease dramatically as soon as λ excited orbitals become populated.

The B_2 and C_2 molecules have small dissociation energies although both are still bound. The value of this energy is only 0.7 Ry for C_2 and one must wonder how this number is affected by numerical inaccuracies and by the

TABLE IV. Atomic (E_A,E_B), molecular (E_{AB}), total energies and dissociation energies (E_D) in Rydbergs and "equilibrium" internuclear distances (R in units of a_0) of ground states of homonuclear diatomic molecules.

	AB	R	E_{AB}	A	E_A	B	E_B	E_A+E_B	E_D[a]
H_2	[01]	0.18	−35.8	[0]	−15.2	[1]	−11.2	−26.4	9.4
He_2	[0123]	0.17	−119.5	[01]	−55.4	[23]	−36.3	−91.7	27.8
Li_2	[012345]	0.19	−239.4	[012]	−118.4	[345]	−71.7	−190.1	49.3
Be_2	$[0_2 123456]$	0.26	−401.7	[0123]	−201.9	[0456]	−168.6	−370.5	31.2
B_2	$[0_2 1_2 2_2 3456]$	0.36	−605.2	[01234]	−304.2	[01256]	−292.2	−596.4	8.8
C_2	$[0_2 1_2 2_2 3_2 4_2 56]$	0.50	−845.5	[012345]	−424.3	[012346]	−420.5	−844.8	0.7

[a] $E_D=E_A+E_B-E_{AB}$.

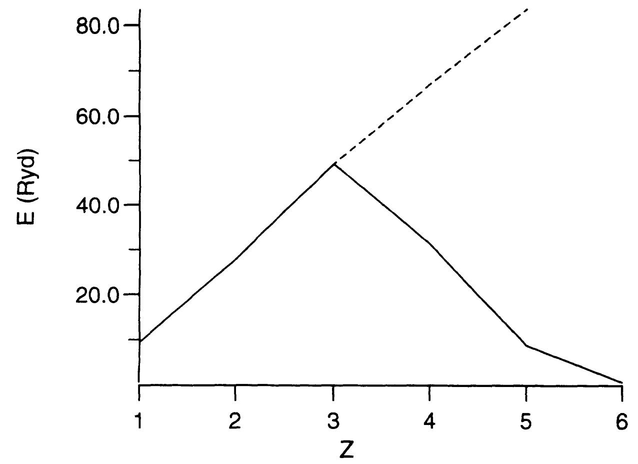

FIG. 1. Variation of the dissociation energies of homonuclear diatomic molecules as a function of the charge of the nucleus. The full line corresponds to the ground-state configurations and the dotted line to a configuration where all the electron wave functions correspond to different values of λ.

mean-field approximation. Both errors lead to an underestimation of E_D. We checked that an increase of the number of integration points or of the Lagrange basis confirms the stability of the molecules and that our numerical accuracy on E_D can be estimated to a few electron volts. Our method being variational, the relative accuracy on the total energies is of the same order of magnitude than the accuracies on their components, although these are much larger (see Table V). To obtain a good numerical precision, it is also essential to compute both the molecule and its atomic dissociation products with the same Lagrange basis. Correlations beyond the Hartree-Fock approximation would, of course, modify both the energies of the molecule and of the dissociation products. However, these correlations are probably larger in the molecular case than in the atomic one. For instance, the $\lambda=0$ electronic wave functions in C_2 break slightly the symmetry with respect to the exchange of the two carbons. The retoration of this symmetry would bring a gain in stability of the order of a few Rydbergs.

TABLE V. Total energies ($E_{\rm tot}$ in Rydbergs) and "equilibrium" interdistances (R in a_0) of low-lying states of B_2. $E_{\rm kin}$, $V_{i\alpha}$, V_{ij}, and $V_{\alpha\beta}$ are the longitudinal kinetic energy, the electron-nuclei, electron-electron, and nucleus-nucleus Coulomb interaction contributions. E_D is the dissociation energy calculated with respect to the most stable partition of the dissociation products.

Configuration	$[0_2 1_2 2_2 \ldots 6]$	$[0_2 1_2 \ldots 7]$	$[01 \ldots 9]$
$R(a_0)$	0.36	0.30	0.19
$E_{\rm kin}$	171.1	164.3	96.3
$V_{i\alpha}$	-1326.5	-1372.7	-1373.0
V_{ij}	411.3	437.2	459.0
$V_{\alpha\beta}$	138.9	166.7	263.2
$E_{\rm tot}$	-605.2	-604.6	-554.5
E_D	8.8	23.9	83.4

Taking all these sources of unaccuracies into account, B_2, which has a dissociation energy of the order of 1% of its total energy, is probably the heaviest molecule that we can predict as being stable with some confidence.

Table V details the total energies of three configurations of the molecule B_2. The selected configurations are the two lowest ones, having, respectively, three and two λ duplications and lying very close to each other, and the simple "stacking up" distribution which lies approximately 40 Ry higher. The total energies result from a delicate balance between the binding contributions due to the nucleus-electron interaction and the antibinding effects due to the three other terms of the Hamiltonian. The increase of R due to the population of λ excited states explains the decrease of the absolute values of the Coulomb terms ($V_{i\alpha}$, V_{ij}, $V_{\alpha\beta}$). In the same time, the longitudinal kinetic energy $E_{\rm kin}=\langle -d^2/dz^2\rangle$ grows slowly, as a consequence of the Pauli exclusion principle. The dissociation energies of the three configurations are very different. The differences are due to the more favorable atomic dissociation limits, resulting from the break-up of a molecule in a configuration having electrons with same λ's.

B. Finite chains H_n and He_n

The most stable configurations of H_n ($n=1,2,\ldots,5$) and He_n ($n=1,\ldots,4$) are presented in Table VI, with their calculated total energies ($E_{\rm tot}$) and equilibrium nuclear interdistances. In the same table, we present the total dissociation energies (E_D) (i.e., the energies of atomization) of H_n and He_n calculated from the sum of the atomic total energies (Σ), corresponding to the dissociation partition specified in the 5th column.

In his study of infinite nuclear chains, Ruderman [1] made the conjecture that the ground-state configuration of H_3 is the configuration $[0_2 1]$. Our results do not support this hypothesis. As mentioned in the Introduction and found by Lai, Salpeter, and Shapiro [9] for H_n ($n \leq 4$), the nuclear charge $Z=1$ is not strong enough to provoke the occurrence of two same λ's at a low energy cost. Our calculations indicate that H_5 is the shortest chain in which a λ excited state is populated. The fact that it already occurs at $n=4$ in the sequence He_n indicates the efficient role of Z in the process, at least when $\gamma=1000$. The population of λ excited states manifests itself in the reduction of the bond energies calculated by dividing the total dissociation energies by the number of chemical bonds ($n-1$). These are reported in the last column of Table VI.

Our total energies are sensitively lower than the -34.82 and -54.94 values found for H_2 and H_3 by Demeur and Mowlavi [16], illustrating the superiority of our Lagrange basis set. Lai, Salpeter, and Shapiro [9] have studied the stability of hydrogen molecules and of H and He chains as a function of the magnetic-field strength. To make a comparison with their results, we have recalculated the H_3 and H_4 molecules at magnetic fields of 10^{12} and 2×10^{12} G. Our results are slightly less accurate than theirs, with a difference of a few tenths of a percent. Increasing the number of Lagrange functions

TABLE VI. Molecular total energies (E_{tot}), dissociation energies (E_D) in Rydberg and "equilibrium" distances (R in a_0) of ground states in H_n ($n=1-5$) and He_n ($n=1-4$) molecular chains at $\gamma=1000$. Σ is the sum over the atomic total energies according to the partition specified in the 5th column. The dissociation energy is calculated from $E_D=\Sigma-E_{\text{tot}}$.

	Configuration	R	E_{tot}	Partition	Σ	E_D	$E_D/(n-1)$
H_2	[01]	0.18	−35.8	$0 \mid 1$	−26.4	9.4	9.4
H_3	[012]	0.16	−56.3	$0 \mid 1 \mid 2$	−36.0	20.3	10.2
H_4	[0123]	0.15	−74.8	$0 \mid 1 \mid 2 \mid 3$	−44.5	30.3	10.1
H_5	$[0_2123]$	0.17	−93.8	$0 \mid 0 \mid 1 \mid 2 \mid 3$	−59.7	34.1	8.5
He_2	[0123]	0.17	−119.5	$01 \mid 23$	−91.7	27.8	27.8
He_3	[012345]	0.17	−175.6	$05 \mid 14 \mid 23$	−121.7	53.9	27.0
He_4	$[0_2123456]$	0.18	−236.8	$05 \mid 14 \mid 23 \mid 06$	−169.3	67.5	22.5

decreases our total energies and brings them still closer to those of Lai, Salpeter, and Shapiro [9].

Neuhauser, Koonin, and Langanke [2] evaluated the cohesion energies of one-dimensional infinite chains. They found that the only *infinite* stable chains are H_∞ and He_∞ at $\gamma=425$ and H_∞, He_∞, Li_∞, and Be_∞ at $\gamma=2125$. The cohesion energies are not directly comparable to the dissociation energies of diatomic molecules or of finite chains. However, as can be seen in Table VI, and has been found by Lai, Salpeter, and Shapiro [9] for hydrogen chains, the total energy of a chain divided by the number of atoms stabilizes very quickly when increasing the number of atoms. The occurrence of two $\lambda=0$ orbitals in the ground state of H_5 strengthens this tendency, the configuration [01234] having an energy per atom which is 0.2 Ry higher. If we subtract from the energy per atom the ground-state energy of the isolated atom, we find for the He chain a value of 61 eV, which lies nicely between the cohesion energies found by Neuhauser, Koonin, and Langanke at γ equal to 425 and 2128 (25 and 150 eV, respectively). However, our calculations show that diatomic molecules can be stable while infinite chains are not. A decrease of the field strength to $\gamma=425$ confirms this result. We have found that the Li_2 and Be_2 molecules are stable at this field, with dissociation energies, respectively, of 30.9 and 9.4 Ry. Therefore, we cannot specify from our calculations the atomic composition of infinite chains which will be unstable.

IV. CONCLUSION

In this work, we have introduced an alternative method to study the stability of molecules immersed in very intense magnetic field. We have shown that the results obtained with this Hartree-Fock on a mesh method can reach the accuracy of the Hartree-Fock results available for atoms. Moreover, our approach avoids the intricate optimization problems encountered in some previous studies of small molecules.

Our main results were presented in Table IV and in Fig. 1. The electronic ground-state configurations of diatomic homonuclear molecules are quite different from that of light atoms, where only nodeless electronic wave functions are populated. With increasing Z, a Hund doublet appears and induces a gerade-ungerade localization of two $\lambda=0$ electrons, a first step in the formation of two individual atoms. Table IV indicates clearly the appearance of such a situation between $Z=3$ and 4. Moreover, the increase of Z leads to new doublets of electrons with larger values of λ.

At $\gamma=1000$, this phenomenon leads to a decrease of the dissociation energy of the molecules beyond Li_2. However, our study shows that molecules up to at least B_2 are stable while the corresponding infinite chains are predicted to be unstable. For C_2, correlation energies are of the same order of magnitude than the dissociation energy and it would be necessary to go beyond the Hartree-Fock approach to get a firm conclusion. This difference between infinite chains and diatomic molecules is confirmed by our calculations performed for a lower value of the magnetic field. It would be interesting to extend the present work to heavier homonuclear molecules and finite chains composed of atoms with Z larger than two, but that would require going beyond the mean-field approximation. We plan to study the stability of some light heteronuclear molecules, including hydrids.

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