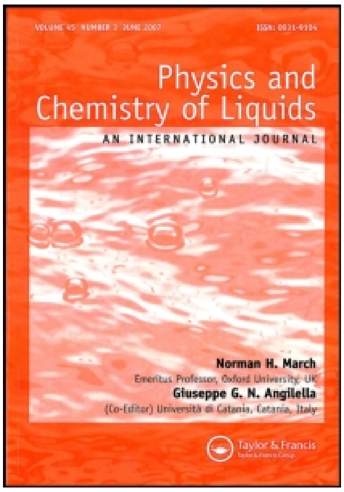

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INHOMOGENEOUS ELECTRON LIQUID IN A HOMOGENEOUS MAGNETIC FIELD OF ARBITRARY STRENGTH

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Our recent paper [*Phys. Rev. A*, **60**, 2853 (1999)] on the field dependence of the energy of a molecule in an arbitrary magnetic field is extended here by results which can be expressed solely in terms of the total kinetic energy of the electron liquid of a molecule or an atom in a homogeneous magnetic field.

Keywords: Magnetic field dependent molecular energy; Virial equation in magnetic field

Very general and exact relations for the energy of the electronic system of a molecule in an arbitrary magnetic field can be obtained by applying to this system the variational principle and the Hellmann–Feynman theorem, as was done in our recent paper [1]. The present Letter represents some extension of this paper by providing results which can be deduced from the virial equation (VE) in the form

$$\left(-R\frac{\partial}{\partial R}+2B\frac{\partial}{\partial B}-1\right)E_{\mathrm{mol}}(R,B)=T(R,B), \tag{1}$$

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which is a combination of Eqs. (4.13b) and (3.9) given in Ref. [1], but not discussed there as a whole. Here T is the total kinetic energy of the electron liquid of a molecule, which, together with E_C – the total Coulombic energy (a sum of electron–electron, electron–nucleus and nucleus–nucleus contributions) gives the total energy of a molecule $E_{mol} = T + E_C$. All terms are functions of B – the magnitude of a homogeneous magnetic field, and R – the size parameter, which characterizes a uniform scaling of a molecule (each bond length is scaled with a factor R, while bond angles, and orientation angles with respect to the field direction, remain unchanged during scaling). It should be noted that T, Eq. (3.10a) in Ref. [1], is given as a sum of explicit expressions, Eqs. (2.5)–(2.8), in terms of the first-order density matrix γ_1 of the system and the magnetic field B along the z axis (*via* the vector potential $\mathbf{A}(\mathbf{r}) = (1/2)(-y, x, 0)\ B$). What is important is that T is a gauge-invariant quantity as shown in Eqs. (A9) and (A5) of Ref. [1].

Let us suppose that the dependence of γ_1 on R and B is known. Then the function $T(R, B)$ is available and $E_{mol}(R, B)$ can be found by solving Eq. (1) as a differential equation. We claim that the unique solution $E_{mol}(R, B)$ passing through the initial condition – the solution at the point $\{R_0, B_0\} = \{R/\zeta_0, B\zeta_0^2\}$ (ζ_0 is a fixed real parameter, $0 < \zeta_0 < \infty$) situated on the line $R'^2B' = \text{const} = R_0^2B_0 = R^2B$ in the $\{R', B'\}$ plane, is given by

$$E_{mol}(R, B) = \zeta_0^{-1}E_{mol}(R/\zeta_0, B\zeta_0^2) + \int_{\zeta_0}^{1} d\zeta\zeta^{-2}T(R/\zeta, B\zeta^2). \qquad (2)$$

The notation for an intermediate point $\{R', B'\} = \{R/\zeta,\ B\zeta^2\}$, for the linear operator $\hat{L}(R, B) = (-R\partial/\partial R + 2B\partial/\partial B - 1)$, and the identities (3) and (4) below which are easily verified:

$$\hat{L}(R, B) = \hat{L}(R', B') = \hat{L}(R_0, B_0), \qquad (3)$$

$$\frac{d}{d\zeta}\{\zeta^{-1}T(R', B')\} = \zeta^{-2}\hat{L}(R', B')T(R', B'), \qquad (4)$$

are helpful for the proof. After inserting the solution (2) into the left-hand side of the VE (1) we obtain

$$\begin{aligned}\hat{L}(R,B)E_{\mathrm{mol}}(R,B) &= \zeta_0^{-1}\hat{L}(R_0,B_0)E_{\mathrm{mol}}(R_0,B_0)+\int_{\zeta_0}^{1} d\zeta\zeta^{-2}\hat{L}(R',B')T(R',B') \\ &= \zeta_0^{-1}T(R_0,B_0)+\int_{\zeta_0}^{1} d\zeta\frac{d}{d\zeta}\{\zeta^{-1}T(R',B')\} \\ &= \zeta_0^{-1}T(R_0,B_0)+\{T(R,B)-\zeta_0^{-1}T(R_0,B_0)\}=T(R,B).\end{aligned} \tag{5}$$

In the first step, the identity (3) was used, in the second step, the VE (1) at the point $\{R_0,B_0\}$ was applied to the first term, while the identity (4) – to the second term, which was integrated in the third step.

Equation (2), when rewritten with explicit $\zeta_0=(B_0/B)^{1/2}$,

$$E_{\mathrm{mol}}(R,B)=(B/B_0)^{1/2}E_{\mathrm{mol}}((B/B_0)^{1/2}R,B_0)+\int_{(B_0/B)^{1/2}}^{1} d\zeta\zeta^{-2}T(R/\zeta,B\zeta^2), \tag{6}$$

represents extrapolation to the field B of the result for the molecular energy known at the field B_0, similar to Eqs. (4.35) – (4.37) in Ref. [1]. Now let us subtract from Eq. (2) its copy taken at $B=0$, and, next, perform the limit $\zeta_0\to 0$. The result

$$E_{\mathrm{mol}}(R,B) = E_{\mathrm{mol}}(R,0) + \int_0^1 d\zeta\zeta^{-2}\{T(R/\zeta,B\zeta^2) - T(R/\zeta,0)\} \tag{7}$$

is so simple, because the term due to initial conditions

$$\begin{aligned}\zeta_0^{-1}\{E_{\mathrm{mol}}(R_0,B_0)-E_{\mathrm{mol}}(R_0,0)\} &= \zeta_0^{-1}\left\{\left.\frac{\partial E_{\mathrm{mol}}(R_0,B'')}{\partial B''}\right|_{B''=0} B_0+O(B_0^2)\right\} \\ &= \left.\frac{\partial E_{\mathrm{mol}}(R/\zeta_0,B'')}{\partial B''}\right|_{B''=0} B\zeta_0^2\zeta_0^{-1}+O(\zeta_0^4\zeta_0^{-1})\end{aligned} \tag{8}$$

vanishes for $\zeta_0\to 0$. The new result (7), although similar to our [1] previous results in Eqs. (4.22), (4.28), (4.33), is more convenient, because it does not involve the magnetization vector (the contributions due to initial conditions – the analogs of Eq. (8) for previous results, lead in the $\zeta_0 \rightarrow 0$ limit to nonzero values, proportional to magnetization).

All molecular results can be easily adapted to the single-atomic case by removing any reference to R, and changing, for consistency, the notation for the total energy of the system from $E_{\mathrm{mol}}(R, B)$ to $E(B)$ (the nucleus–nucleus energy contribution now being absent). Thus, the VE (1), the extrapolating energy, Eq. (6), and the field dependence of the system energy, Eq. (7), all rewritten for an atom, become

$$\left(2B\frac{\partial}{\partial B} - 1\right)E(B) = T(B) \tag{9}$$

(similar to Eqs. (5.5), (5.6) in Ref. [1]),

$$E(B) = (B/B_0)^{1/2}E(B_0) + \int_{(B_0/B)^{1/2}}^{1} d\zeta\zeta^{-2}T(B\zeta^2) \tag{10}$$

(similar to Eq. (5.11)), and

$$E(B) = E(0) + \int_0^1 d\zeta\zeta^{-2}\{T(B\zeta^2) - T(0)\}, \tag{11}$$

(similar to Eqs. (5.9), (5.10)).

It is worth reminding the reader that all results obtained in Ref. [1] and, therefore, the results obtained in the present Letter, are valid for magnetic field B of arbitrary strength, are applicable to any eigenenergy of the system (including the ground state) not only in the case of exact solutions, but also for a wide class of approximate solutions and in particular, from the Hartree–Fock method.

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Reference

[1] Holas, A. and March, N. H. (1999). *Phys. Rev. A*, **60**, 2853.