The magnetic two-centre problem: some rigorous properties

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Abstract

We study the quantum mechanical magnetic two-centre problem, i.e., quantum states of an electron within the Coulomb field of two fixed nuclear centres and a homogeneous magnetic field. From the corresponding nonrelativistic Schrödinger equation various characteristic properties are derived. These include the ordering of energy levels and the monotonicity of electronic energies as a function of the nuclear separation if the internuclear axis is parallel to the direction of the **B** field. For such situations we also obtain lower bounds on the equilibrium separation between the nuclei and establish decay properties of bound state wavefunctions. Moreover, the molecular virial theorem is generalized to encompass the contributions from the magnetic field.

PACS numbers: 02.30.Tb, 03.65.Db, 31.10.+z, 33.15.−e

1. Introduction

The hydrogen molecular ion, or, more generally, one electron interacting with two (fixed) nuclear centres via the Coulomb potential, embodies the simplest molecular system. Therefore it often serves as the candidate of choice for precise qualitative and quantitative studies of the molecular bond [1–3]. Also if one considers the effect of external (magnetic, in particular) fields on molecular binding, this system allows detailed and accurate calculations (see the recent review [4] and references therein). In fact, the bulk of the theoretical knowledge on molecules in magnetic fields accumulated so far is based on numerical investigations; rigorous information usually pertains only to asymptotic regimes, as, e.g., semiclassics or large field strengths [5–8]. Here, focusing onto the two-centre one-electron system and homogeneous magnetic fields **B**, our aim is to demonstrate various rigorous results describing the behaviour of electronic energies, of potential energy curves (PECs), and of eigenfunctions.

More specifically, assuming the Born–Oppenheimer ('clamped nuclei') approximation (cf, e.g., [9–11] for a discussion of its validity), in the subsequent section 2 we define the corresponding nonrelativistic Schrödinger operator $H[\mathbf{R}, \mathbf{B}, Z_1, Z_2]$ that depends on the internuclear separation (vector) $\mathbf{R}$, the magnetic field $\mathbf{B}$, and the nuclear charges Z_1, Z_2. The Hamiltonian H does not include spin, but is equivalent—up to a trivial term—to the Pauli operator $H + \sigma \cdot \mathbf{B}$ (where σ stands for the collection of Pauli matrices). If $\mathbf{R} \wedge \mathbf{B} = 0$, i.e., $\mathbf{R}$ is parallel to $\mathbf{B}$, the system is invariant under rotations around the internuclear axis and the associated angular momentum a constant of motion. This leads to reduced Hamilton operators H_m for each 'magnetic' quantum number m with the magnetic part of H_m essentially given by a harmonic oscillator potential. Although for $\mathbf{B} \neq 0$ a separation of the remaining two degrees of freedom in H_m is no longer possible, choosing coordinates along and orthogonal to the field direction proves to be advantageous for the analysis of these operators. In this context, we also show the positivity of the lowest eigenfunctions of H_m for each m-sector.

One of the important tools of atomic and molecular theory is the virial theorem, but apparently it has not yet been extended to atomic or molecular systems in a magnetic field. To do so, in section 3 we examine the scaling properties of the two-centre Hamiltonians with respect to their parameters. As a result, a virial theorem emerges that can be regarded as a combination of the virial formulae for Coulomb and harmonic oscillator systems and that generalizes the usual molecular virial theorem to the situation $\mathbf{B} \neq 0$.

Section 4 is devoted to the problem of level ordering for varying m. For one-electron atoms it is known [12] that also for nonvanishing (homogeneous) magnetic fields the ground state occurs for angular momentum $m = 0$. For one-electron two-centre systems, we show that a strategy originally put forward by Gross and Stubbe [13] can be adapted and reformulated with the help of commutators; whence, if one compares corresponding energy levels for $|m|$ and $|m| + 1$, we show that the former cannot exceed the latter.

Since in a homogeneous field there are no forces along the direction of $\mathbf{B}$, one may expect certain related attributes of molecular states to remain valid independent of the presence or absence of the external field. In particular, for the ground state and $\mathbf{B} = 0$, the electronic curves have been demonstrated to increase monotonically with growing nuclear separation [14–16]. The monotonic behaviour of the electronic energies for a class of excited states, namely, the lowest state for each quantum number m, has been established later [17]. In section 5, we employ the same arguments as in the field-free case to extend this monotonicity also to $\mathbf{B} \neq 0$.

The monotonicity of the electronic energies is exploited in section 6 to derive further properties of the system. We point out immediate consequences for the behaviour of (vertical) ionization energies, and prove the convergence of a class of electronic curves in the separated atoms limit (SAL), namely, as $|\mathbf{R}| \to \infty$. Furthermore, by a straightforward argument, lower bounds on the equilibrium separation for the corresponding PECs are deduced and compared with asymptotic (large $|\mathbf{B}|$) results [8] and numerical data [18].

Decay of bound state wavefunctions is the subject of section 7. Invoking standard methods (Combes–Thomas [19], Agmon [20]), we show that the transversal decay is governed by the behaviour of the Landau orbital, whereas along the field direction the decay characteristics are the same as for molecular wavefunctions without magnetic field.

Finally, various concluding remarks are collected in section 8.

2. Basic properties of the magnetic Hamiltonian

Assuming static nuclei with charges $Z_1, Z_2 \geqslant 0$, we consider the Hamiltonian $H[\mathbf{R}, \mathbf{B}, Z_1, Z_2] = h[\mathbf{R}, \mathbf{B}, Z_1, Z_2] + Z_1 Z_2 / R$ where for a homogeneous magnetic field $\mathbf{B}$ the

electronic part h of H is determined by

$$h[\mathbf{R}, \mathbf{B}, Z_1, Z_2] = \tfrac{1}{2}\mathbf{p}^2 + \tfrac{1}{2}\mathbf{B}\cdot\mathbf{L} + \tfrac{1}{8}B^2 r_\perp^2 + V(\mathbf{R}, Z_1, Z_2). \tag{1}$$

Here, $\mathbf{L} = \mathbf{r} \wedge \mathbf{p}$ stands for the usual angular momentum operator, and $r_\perp$ is the component of $\mathbf{r}$ orthogonal to $\mathbf{B}$, namely, $r_\perp^2 = r^2 - (\mathbf{B}\cdot\mathbf{r})^2/B^2$. The potential V describes the interaction between the electron and the nuclei at positions 0 and $\mathbf{R}$,

$$V[\mathbf{R}, Z_1, Z_2] = -\frac{Z_1}{|\mathbf{r}|} - \frac{Z_2}{|\mathbf{r} - \mathbf{R}|}. \tag{2}$$

If the nuclear axis is oriented along the direction of the field, i.e., $\mathbf{R} \wedge \mathbf{B} = 0$, the system enjoys symmetry $\mathcal{C}_{\infty v}$ (or $\mathcal{D}_{\infty h}$, if $Z_1 = Z_2$), and the angular motion can be separated from the remaining two degrees of freedom for the electron. To this end, taking $\mathbf{B} = (0, 0, B)$, $\mathbf{R} = (0, 0, R)$, the usual cylindrical coordinates (ρ, ζ, φ) are introduced by the diffeomorphism $\Phi_{\mathrm{cy}} : \Omega \times S^1 := (0, \infty) \times (-\infty, \infty) \times [0, 2\pi) \longrightarrow \mathbb{R}^3 \setminus \{(0, 0, z) | z \in \mathbb{R}\}$ defined by $\Phi_{\mathrm{cy}}(\rho, \zeta, \varphi) = (\rho\cos(\varphi), \rho\sin(\varphi), \zeta)$. The map Φ_{cy} induces the unitary transformation

$$U_{\mathrm{cy}} : L^2(\mathbb{R}^3) \to L^2(\Omega, \mathrm{d}\omega) \otimes L^2(S^1), \qquad \psi_1 \mapsto \psi_2 = U_{\mathrm{cy}}\psi_1 := \psi_1 \circ \Phi_{\mathrm{cy}}, \tag{3}$$

between the Hilbert spaces $L^2(\mathbb{R}^3)$ and $L^2(\Omega, \mathrm{d}\omega) \otimes L^2(S^1, \mathrm{d}\varphi)$ with measure $\mathrm{d}\omega = \rho\,\mathrm{d}\rho\,\mathrm{d}\zeta$. The Hamiltonian h is then unitarily transformed into

$$h_{\mathrm{cy}} := U_{\mathrm{cy}} h U_{\mathrm{cy}}^{-1} = h_\perp + h_\parallel - \frac{1}{2\rho^2}\frac{\partial^2}{\partial\varphi^2} + \frac{i}{2}B\frac{\partial}{\partial\varphi} + \frac{1}{8}B^2\rho^2 + v, \tag{4}$$

where we use the notation $h_\perp = -\tfrac{1}{2}\rho^{-1}\frac{\partial}{\partial\rho}\rho\frac{\partial}{\partial\rho}$, $h_\parallel = -\tfrac{1}{2}\frac{\partial^2}{\partial\zeta^2}$, and

$$v[R, Z_1, Z_2] = -\frac{Z_1}{\sqrt{\rho^2 + \zeta^2}} - \frac{Z_2}{\sqrt{\rho^2 + (\zeta - R)^2}}. \tag{5}$$

Decomposing $L^2(\Omega, \mathrm{d}\omega) \otimes L^2(S^1) = \bigoplus_{m \in \mathbb{Z}} L^2(\Omega, \mathrm{d}\omega) \otimes \mathcal{L}(Y_m)$ with $\mathcal{L}(Y_m)$ being the linear span of the angular momentum eigenfunctions $Y_m(\varphi) = \exp(im\varphi)$, the Hamiltonian is reduced on each eigenspace of fixed angular momentum $m \in \mathbb{Z}$ around the internuclear axis

$$h_{\mathrm{cy}} = \bigoplus_{m \in \mathbb{Z}} h_{\mathrm{cy}}^{(m)} = \bigoplus_{m \in \mathbb{Z}} \left(h_\perp + \frac{m^2}{2\rho^2} + h_\parallel - \frac{m}{2}B + \frac{1}{8}B^2\rho^2 + v \right). \tag{6}$$

For the subsequent discussion it will be convenient to single out the magnetic part of the Hamiltonian,

$$h_{\mathrm{cy}}^{(m)} = h_{\mathrm{mag}}^{(m)} + v, \quad h_{\mathrm{mag}}^{(m)}[B] = h_\perp^{(m)} + h_\parallel - \frac{m}{2}B + \frac{1}{8}B^2\rho^2, \quad h_\perp^{(m)} = h_\perp + \frac{m^2}{2\rho^2}. \tag{7}$$

Obviously, $h_{\mathrm{mag}}^{(m)}[B]$ models a harmonic oscillator in ρ and free motion in ζ direction. The essential selfadjointness of $h_{\mathrm{mag}}^{(m)}[0]$ on appropriate domains $\mathcal{D}_m \otimes C_0^\infty(\mathbb{R})$ (with $\mathcal{D}_m \subset C^\infty(\mathbb{R}^+)$) has been established in [17]. These results can be extended to $h_{\mathrm{mag}}^{(m)}[B]$ for nonvanishing B by standard methods; moreover, using that $h_{\mathrm{mag}}^{(m)}[B]$ induces a finer topology than $h_{\mathrm{mag}}^{(m)}[0]$ for the graph norm, the relative compactness of $v \in L^2(\Omega, \mathrm{d}\omega) + L_\epsilon^\infty(\Omega)$ and thus the essential selfadjointness of $h_{\mathrm{cy}}^{(m)}$ on $\mathcal{D}_m \otimes C_0^\infty(\mathbb{R})$ follow. The ground state energies e_m and wavefunctions ϕ_m of $h_{\mathrm{cy}}^{(m)}$ enjoy a particular property:

Theorem 2.1. *The ground state wavefunction of $h_{\mathrm{cy}}^{(m)}$ is strictly positive, $\phi_m(\rho, \zeta) > 0$ for all $\rho > 0$, $-\infty < \zeta < \infty$, and the ground state energy e_m nondegenerate.*

Whereas sometimes the positivity of ϕ_m is alluded to a 'generalized Frobenius Perron theorem', the actual proof involves several steps and apparently has not yet been documented in the literature. First, we generalize Kato's inequality (theorem X.27 in [21]) to the kinetic part of $h_{\text{cy}}^{(m)}$, i.e., show that that in distributional sense

$$\left(-\rho^{-1} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} - \frac{\partial^2}{\partial \zeta^2} \right) |\phi| \leqslant -\text{Re} \left\{ \text{sgn}(\phi) \left(-\rho^{-1} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} - \frac{\partial^2}{\partial \zeta^2} \right) \phi \right\}, \tag{8}$$

where $\text{sgn}(\phi) = 0$ if $\phi(\rho, \zeta) = 0$, and $\text{sgn}(\phi) = \overline{\phi}(\rho, \zeta)/|\phi(\rho, \zeta)|$ otherwise. Hence, the condition $\langle |\phi|, h_{\text{mag}}^{(m)} |\phi| \rangle \leqslant \langle \phi, h_{\text{mag}}^{(m)} \phi \rangle$ for the first Beurling–Deny criterion (theorem XIII.50 in [22]) is satisfied; as a consequence, the semigroup $\exp\left(-t h_{\text{mag}}^{(m)}\right), t > 0$, is positivity preserving, that is, $\phi \geqslant 0$ a.e. implies $\exp\left(-t h_{\text{mag}}^{(m)}\right)\phi \geqslant 0$ a.e. Moreover, $\left\{\exp\left(-t h_{\text{mag}}^{(m)}\right)\right\} \cup L^\infty(L^2)$ acts irreducibly, i.e., only the trivial closed subspaces of $L^2(\Omega, d\omega)$ are left invariant by $\exp\left(-t h_{\text{mag}}^{(m)}\right)$ and all bounded operators. This can be deduced by the same reasoning as in theorem XIII.43 of [22] from the ergodicity, i.e., $\langle \psi, \exp\left(-s h_{\text{mag}}^{(m)}\right)\phi \rangle \neq 0$ for all positive $\psi, \phi \in L^2(\Omega, d\omega)$ and some $s > 0$. The latter, in turn, can be seen by employing the Trotter formula and the respective properties of the kernels of the resulting factors. Next, we approximate the potential v by the bounded operators

$$v_n(\rho, \zeta) := \begin{cases} -n & \text{if } v(\rho, \zeta) < -n, \\ v(\rho, \zeta) & \text{otherwise.} \end{cases} \tag{9}$$

Easy estimates of $\langle \phi, |v - v_n| \phi \rangle$ for $\phi \in \mathcal{D}\left(h_{\text{mag}}^{(m)}\right) = \mathcal{D}\left(h_{\text{cy}}^{(m)}\right)$ and theorem VIII.25 in [23] prove the convergence in norm resolvent sense $h_{\text{mag}}^{(m)} + v_n \to h_{\text{cy}}^{(m)}$ and $h_{\text{cy}}^{(m)} - v_n \to h_{\text{mag}}^{(m)}$ for $n \to \infty$. Whence, by theorem XIII.45 of [22], the facts that $\exp\left(-t h_{\text{mag}}^{(m)}\right)$ is positivity preserving and $\left\{\exp\left(-t h_{\text{mag}}^{(m)}\right)\right\} \cup L^\infty(L^2)$ acts irreducibly are inherited to $\exp\left(-t h_{\text{cy}}^{(m)}\right)$. This eventually allows us to deduce the strict positivity of ϕ_m and nondegeneracy of e_m from theorems XIII.44 and 45 of [22].

3. Scaling and the virial theorem

To investigate the scaling properties of the magnetic two-centre Hamiltonian we resort to the unitary map ('dilation') $U_a : L^2(\mathbb{R}^3) \to L^2(\mathbb{R}^3)$ given by $U_a \psi(\mathbf{r}) = a^{-3/2} \psi(a\mathbf{r})$ for all $a \in \mathbb{R}^+$. With $\hat{\mathbf{R}} = \mathbf{R}/R$ standing for the unit vector along the internuclear axis, the scaling in R produces

$$U_R h U_R^{-1} = R^{-2} \left(-\frac{1}{2}\Delta + \frac{1}{2}R^2 \mathbf{B} \cdot \mathbf{L} + \frac{1}{8}R^4 B^2 r_\perp^2 - \frac{R Z_1}{|\mathbf{r}|} - \frac{R Z_2}{|\mathbf{r} - \hat{\mathbf{R}}|} \right). \tag{10}$$

For the electronic energies this implies $e[\mathbf{R}, \mathbf{B}, Z_1, Z_2] = R^{-2} e[\hat{\mathbf{R}}, R^2 \mathbf{B}, R Z_1, R Z_2]$. Furthermore, equation (10) leads to a molecular virial theorem in the following way. If ψ is any eigenstate of h, then $\tilde{\psi} = U_R \psi$ is an eigenstate of the transformed operator $U_R h U_R^{-1}$. Therefore we can apply the Feynman–Hellman theorem for the derivative (in the direction of $\hat{\mathbf{R}}$) of the corresponding energy e

$$\frac{de}{dR} = \left\langle \tilde{\psi}, \left(\frac{d}{dR} U_R h U_R^{-1} \right) \tilde{\psi} \right\rangle. \tag{11}$$

The derivative of the operator is calculated with the help of (10)

$$\frac{d}{dR} U_R h U_R^{-1} = -2R^{-1} U_R h U_R^{-1} + R^{-1} U_R \left(\frac{2}{2}\mathbf{B} \cdot \mathbf{L} + \frac{4}{8}B^2 r_\perp^2 - \frac{Z_1}{r} - \frac{Z_2}{|\mathbf{r} - \mathbf{R}|} \right) U_R^{-1}, \tag{12}$$

so that

$$R\frac{\mathrm{d}e}{\mathrm{d}R} = -2e + \left\langle \psi, \left(\mathbf{B}\cdot\mathbf{L} + \frac{1}{2}B^2 r_\perp^2 - \frac{Z_1}{r} - \frac{Z_2}{|\mathbf{r}-\mathbf{R}|} \right)\psi \right\rangle. \tag{13}$$

Denoting expectation values with respect to ψ by

$$\langle T \rangle = \left\langle \psi, -\frac{1}{2}\Delta\psi \right\rangle, \qquad \langle V \rangle = \left\langle \psi, \left(-\frac{Z_1}{r} - \frac{Z_2}{|\mathbf{r}-\mathbf{R}|} \right)\psi \right\rangle, \tag{14}$$

equation (13) can equivalently be expressed by the two versions below

$$R\frac{\mathrm{d}e}{\mathrm{d}R} = -2e + \langle \mathbf{B}\cdot\mathbf{L}\rangle + \frac{1}{2}B^2\langle r_\perp^2\rangle + \langle V\rangle$$
$$= -e - \langle T\rangle + \frac{1}{2}\langle \mathbf{B}\cdot\mathbf{L}\rangle + \frac{3}{8}B^2\langle r_\perp^2\rangle. \tag{15}$$

In addition, we may reformulate (15) for potential energy curves (PECs), namely, for the energies $E = e + Z_1 Z_2/R$ of the total Hamiltonian H,

$$R\frac{\mathrm{d}E}{\mathrm{d}R} = -2E + \langle \mathbf{B}\cdot\mathbf{L}\rangle + \frac{1}{2}B^2\langle r_\perp^2\rangle + \langle V_{\text{tot}}\rangle + \frac{Z_1 Z_2}{R}$$
$$= -E - \langle T\rangle + \frac{1}{2}\langle \mathbf{B}\cdot\mathbf{L}\rangle + \frac{3}{8}B^2\langle r_\perp^2\rangle, \tag{16}$$

where the total potential $V_{\text{tot}} = V + \frac{Z_1 Z_2}{R}$ includes the nuclear repulsion. At equilibrium positions R_e determined by $\frac{\mathrm{d}E}{\mathrm{d}R}[R_e, B, Z_1, Z_2] = 0$, the virial relation (16) yields

$$2\langle T\rangle = -\langle V_{\text{tot}}\rangle - \frac{Z_1 Z_2}{R_e} + \frac{1}{4}B^2\langle r_\perp^2\rangle. \tag{17}$$

We summarize our findings into the molecular virial theorem (that reduces to the usual one [24] if $\mathbf{B} = 0$).

Theorem 3.1. *For $R > 0$, the electronic curves $e[R, B, Z_1, Z_2]$ and PECs $E[R, B, Z_1, Z_2]$ obey equations (15) and (16), respectively. At molecular equilibria, the balance between kinetic and potential parts of the energy is described by equation (17). In the case of $\mathcal{C}_{\infty v}$ or $\mathcal{D}_{\infty h}$ symmetry, all these relations also hold for the reduced operators $h_{\text{cy}}^{(m)}$ and energies e_m or E_m, respectively, where V is replaced by v and $\langle \mathbf{B}\cdot\mathbf{L}\rangle$ becomes mB.*

The transformation in equation (10) corresponds to the scaling $\mathbf{r} \mapsto R\mathbf{r}$. With $\hat{\mathbf{B}} = \mathbf{B}/|\mathbf{B}|$ denoting the unit vector in field direction, we also can scale $\mathbf{r} \mapsto B^{-1/2}\mathbf{r}$ to obtain

$$U_{1/\sqrt{B}}hU_{1/\sqrt{B}}^{-1} = B\left(-\frac{1}{2}\Delta + \frac{1}{2}\hat{\mathbf{B}}\cdot\mathbf{L} + \frac{1}{8}r_\perp^2 - \frac{B^{-1/2}Z_1}{|\mathbf{r}|} - \frac{B^{-1/2}Z_2}{|\mathbf{r}-B^{1/2}\mathbf{R}|} \right) \tag{18}$$

and $e[\mathbf{R}, B, Z_1, Z_2] = Be[\sqrt{B}\mathbf{R}, \hat{\mathbf{B}}, Z_1/\sqrt{B}, Z_2/\sqrt{B}]$ for the electronic energies. The expression in (18) indicates that the molecular interaction gets ever weaker in the Landau regime, namely, for large B. Moreover, we can follow the same procedure as above to derive an equation for $B\,\mathrm{d}e/\mathrm{d}B$. But since $\mathrm{d}e/\mathrm{d}B = \langle \hat{\mathbf{B}}\cdot\mathbf{L}\rangle/2 + B\langle r_\perp^2\rangle/4$, it turns out that the resulting relation is identical to equation (15). Thus only for $R = 0$ this path leads to a new result, namely to an extension of the virial theorem to the atomic situation

$$2\langle T\rangle = -\langle V\rangle + \frac{1}{4}B^2\langle r_\perp^2\rangle. \tag{19}$$

Finally, it is also possible to use the charge parameters for scaling. Taking, e.g., Z_1, the scaling $\mathbf{r} \mapsto Z_1^{-1}\mathbf{r}$ transforms the operator into

$$U_{1/Z_1}hU_{1/Z_1}^{-1} = Z_1^2\left(-\frac{1}{2}\Delta + \frac{1}{2}Z_1^{-2}\mathbf{B}\cdot\mathbf{L} + \frac{1}{8}(Z_1^{-2}B)^2 r_\perp^2 - \frac{1}{|\mathbf{r}|} - \frac{Z_1^{-1}Z_2}{|\mathbf{r}-Z_1\mathbf{R}|} \right). \tag{20}$$

Consequently, the electronic energies obey $e[\mathbf{R}, \mathbf{B}, Z_1, Z_2] = Z_1^2 e[Z_1\mathbf{R}, \mathbf{B}/Z_1^2, 1, Z_2/Z_1]$. For atomic systems, this reduces to the well-known behaviour $e[0, \mathbf{B}, Z, 0] = Z^2 e[0, \mathbf{B}/Z^2, 1, 0]$.

4. Level ordering

Since for vanishing magnetic field the Hamiltonians obey the operator inequality

$$h_{\text{cy}}^{(|m|+1)}[R, 0, Z_1, Z_2] > h_{\text{cy}}^{(|m|)}[R, 0, Z_1, Z_2] = h_{\text{cy}}^{(-|m|)}[R, 0, Z_1, Z_2], \qquad (21)$$

the min–max principle implies the same ordering for the spectra of these operators. Physically, one may expect that, at least for the ground state energies e_m, the relation

$$e_{|m|+1}[R, B, Z_1, Z_2] > e_{|m|}[R, B, Z_1, Z_2] \qquad (22)$$

continues to hold also for nonzero B. In the UAL, namely, for $R = 0$, this is known to be true [12]. The proof given in the atomic case, however, requires monotonicity of the potential v also in $|\zeta|$ and thus cannot be extended to $R > 0$ (cf [9] for an example where the ground state occurs for $m \neq 0$). On the other hand, one can infer the ordering (22) for molecular levels from trivial extensions (to potentials with singularities at the nuclear positions) of results by Grosse and Stubbe [13]. Falling back onto commutator methods, below we succeed in simplifying and shortening Grosse and Stubbe's original proof.

Theorem 4.1. *For the lowest eigenvalues e_m of the operators $h_{\text{cy}}^{(m)}$ in (6) to satisfy inequality (22), it is sufficient that the potential v increases in the direction orthogonal to $\mathbf{B}$, i.e., $\partial V/\partial\rho \geqslant 0$. In particular, the lowest energies of the Hamiltonian h_{cy} occur for $m = 0$.*

To prove this theorem, we first note that due to $e_{-|m|} = e_{|m|} + |m|B$ we only need to consider $m \geqslant 0$. Furthermore, setting $\tilde{h}_{\text{cy}} = h_{\text{cy}} - (\text{i}/2)B\partial/\partial\varphi$, both operators have identical eigenfunctions ψ_m with corresponding eigenvalues related by

$$h_{\text{cy}}\psi_m = e_m\psi_m = \left(\tilde{h}_{\text{cy}} + \frac{\text{i}}{2}B\frac{\partial}{\partial\varphi}\right)\psi_m = \left(\tilde{e}_m - \frac{m}{2}B\right)\psi_m. \qquad (23)$$

The computation of the commutators

$$\left[\tilde{h}_{\text{cy}}, \cos\varphi\frac{\partial}{\partial\rho} - \rho^{-1}\sin\varphi\frac{\partial}{\partial\varphi}\right] = -\cos\varphi\left(\frac{1}{4}B^2\rho + \frac{\partial v}{\partial\rho}\right) \qquad (24)$$

and

$$[\tilde{h}_{\text{cy}}, \rho\cos\varphi] = -\left(\cos\varphi\frac{\partial}{\partial\rho} - \rho^{-1}\sin\varphi\frac{\partial}{\partial\varphi}\right) \qquad (25)$$

is straightforward; they are well defined on eigenfunctions, whence we can evaluate them between ψ_{m+1} and ψ_m. Upon combining, we immediately arrive at

$$(\tilde{e}_{m+1} - \tilde{e}_m)^2\langle\psi_{m+1}, \rho\cos\varphi\psi_m\rangle = \left\langle\psi_{m+1}, \cos\varphi\left(\frac{1}{4}B^2\rho + \frac{\partial v}{\partial\rho}\right)\psi_m\right\rangle. \qquad (26)$$

After expressing the $\psi_m = \exp(\text{i}m\varphi)\phi_m$ in terms of the eigenfunctions ϕ_m of $h_{\text{cy}}^{(m)}$, integrating over φ, and employing (23), the equation (26) is cast into

$$(e_{m+1} - e_m)(e_{m+1} - e_m + B)\langle\phi_{m+1}, \rho\phi_m\rangle = \left\langle\phi_{m+1}, \frac{\partial v}{\partial\rho}\phi_m\right\rangle. \qquad (27)$$

The lower bound

$$
\begin{aligned}
e_{m+1} = \langle \phi_{m+1}, h_{cy}^{(m+1)} \phi_{m+1} \rangle &= \left\langle \phi_{m+1}, \left(h_{cy}^{(m)} + \frac{2m+1}{\rho^2} - \frac{B}{2} \right) \phi_{m+1} \right\rangle \\
&\geqslant e_m + \left\langle \phi_{m+1}, \frac{2m+1}{\rho^2} \phi_{m+1} \right\rangle - \frac{B}{2}
\end{aligned}
\tag{28}
$$

follows from the variational principle and shows that $e_{m+1} - e_m + B/2 > 0$. Since for the potential v in (5) $\partial v / \partial \rho \geqslant 0$ for all ρ, ζ and $\langle \phi_{m+1}, \rho \phi_m \rangle > 0$ due to the positivity of the ground state eigenfunctions, we conclude from equation (27) that $e_{m+1} - e_m > 0$.

5. Monotonicity in R

Before demonstrating the monotonicity of the electronic curves e_m, we show that not only for $B = 0$ [24], but also for $B \neq 0$ the molecular energies cannot drop below the UAL energy of the ground state.

Theorem 5.1. *All (ground state or excited state) energies $\hat{e}[\mathbf{R}, \mathbf{B}, Z_1, Z_2]$ of the electronic Hamiltonian h are bounded below by the UAL ground state energy, $\hat{e}[\mathbf{R}, \mathbf{B}, Z_1, Z_2] \geqslant e[0, \mathbf{B}, Z_1, Z_2]$. If the system enjoys symmetry $\mathcal{C}_{\infty v}$ or $\mathcal{D}_{\infty h}$, then within each angular momentum sector the UAL energies $e_m[0, B, Z_1, Z_2]$ provide lower bounds on all other energies $\hat{e}_m[R, B, Z_1, Z_2]$ of the reduced operator $h_{cy}^{(m)}$.*

These bounds follow directly from the translational invariance of the kinetic energy and the min–max principle. Namely, if $U_{\mathbf{a}}^t \psi(\mathbf{r}) := \psi(\mathbf{r} - \mathbf{a})$ stands for the unitary translation operator by $\mathbf{a} \in \mathbb{R}^3$, then we can write $h[\mathbf{R}, \mathbf{B}, Z_1, Z_2] = \frac{1}{2} h[0, \mathbf{B}, Z_1, Z_2] + \frac{1}{2} U_{\mathbf{R}}^t h[0, \mathbf{B}, Z_1, Z_2] (U_{\mathbf{R}}^t)^{-1}$. By the min–max principle for the spectrum $\sigma(h)$ of h,

$$
\begin{aligned}
\hat{e}[\mathbf{R}, \mathbf{B}, Z_1, Z_2] &\geqslant \inf\{\sigma(h[\mathbf{R}, \mathbf{B}, Z_1, Z_2])\} \geqslant \frac{1}{2} \inf\{\sigma(h[0, \mathbf{B}, Z_1, Z_2])\} \\
&+ \frac{1}{2} \inf \left\{ \sigma \left(U_{\mathbf{R}}^t h[0, \mathbf{B}, Z_1, Z_2] (U_{\mathbf{R}}^t)^{-1} \right) \right\} = e[0, \mathbf{B}, Z_1, Z_2].
\end{aligned}
\tag{29}
$$

Since the same arguments apply for the reduced energies e_m, theorem 5.1 is proved.

Stronger results can be derived for the lowest energies e_m within each angular momentum sector for $\mathcal{C}_{\infty v}$ or $\mathcal{D}_{\infty h}$ symmetries. To do so, namely, to establish the monotonic increase of e_m with growing R, we may adhere to the same strategy as in [17]. Nonetheless, below we include the essential steps to keep the presentation selfcontained, and, also, to take advantage of some slight simplifications as compared to the original proof. Our starting point is the kernel of the semigroup for $t > 0$

$$
K_t(\rho, \zeta, \rho', \zeta') = e^{-t h_{cy}^{(m)}} (\rho, \zeta; \rho', \zeta').
\tag{30}
$$

Decomposing the Hamiltonian as $h_{cy}^{(m)} = h_{mag}^{(m)}[0] + W^{(m)}$ where now $W^{(m)}$ also contains the terms with B, in order to utilize the Trotter formula we need to regularize the Coulomb singularity in $W^{(m)}$. Thus, after introducing

$$
W_\varepsilon^{(m)}(\rho, \zeta) = -\frac{m}{2} B + \frac{1}{8} B^2 \rho^2 - \frac{Z_1}{\sqrt{\rho^2 + \zeta^2 + \varepsilon^2}} - \frac{Z_2}{\sqrt{\rho^2 + (\zeta - R)^2 + \varepsilon^2}}
\tag{31}
$$

we can express the semigroup by an infinite product

$$
e^{-t h_{cy}^{(m)}} = \lim_{\varepsilon \to 0} \lim_{n \to \infty} \left(e^{-\frac{t}{n} h_{mag}^{(m)}[0]} e^{-\frac{t}{n} W_\varepsilon^{(m)}} \right)^n = \lim_{\varepsilon \to 0} \lim_{n \to \infty} \left(e^{-\frac{t}{n} h_\perp^{(m)}} e^{-\frac{t}{n} h_\parallel} e^{-\frac{t}{n} W_\varepsilon^{(m)}} \right)^n
\tag{32}
$$

As in [16], the Coulomb potential is represented by the Laplace transform of a positive measure $d\mu$

$$e^{\frac{t}{n}Z_1\sqrt{\rho^2+\zeta^2+\varepsilon^2}} = \int d\mu\left(\tau; \frac{t}{n}Z_1\right)e^{-\tau(\rho^2+\zeta^2\varepsilon^2)} = \int d\mu_\varepsilon\left(\tau; \frac{t}{n}Z_1\right)e^{-\tau(\rho^2+\zeta^2)} \tag{33}$$

where $d\mu_\varepsilon = \exp(-\varepsilon^2)\,d\mu$, and where, of course, an analogous formula holds for the term with Z_2 in (31). The kernel of $\exp\left(-\frac{t}{n}h_\parallel\right)$ is Gaussian, $\exp\left(-\frac{t}{n}h_\parallel\right)(\zeta, \zeta') = (4\pi t/n)^{-1/2}\exp(-n(\zeta - \zeta')^2/(4t))$, and the other kinetic contribution obeys $\exp\left(-\frac{t}{n}h_\perp^{(m)}\right)(\rho, \rho') \geqslant 0$ [17]. Whence, upon insertion, the nth approximation for the kernel of the (regularized) semigroup assumes the form

$$K_t^{(\varepsilon,n)}(\rho, \zeta, \rho', \zeta') = \int \prod_{i=1}^{n-1}d\rho_i \int \prod_{j=1}^{n-1}d\zeta_j \int \prod_{k=1}^{n}d\mu_\varepsilon\left(\tau_k; \frac{t}{n}Z_1\right)$$

$$\times \int \prod_{l=n+1}^{2n}d\mu_\varepsilon\left(\tau_l; \frac{t}{n}Z_2\right)F_t^{(n)}(\{\rho\}, \{\tau\})G_t^{(\varepsilon,n)}(\{\zeta\}, \{\tau\}). \tag{34}$$

Here, $\{\rho\} = \rho, \rho_1, \ldots \rho_{n-1}, \rho'$, $\{\zeta\} = \zeta, \zeta_1, \ldots \zeta_{n-1}, \zeta'$, and $\{\tau\}$ stands for the collection of τ_i, $i = 1, \ldots, 2n$. The function $F_t^{(n)}$ in (34)

$$F_t^{(n)}(\{\rho\}, \{\tau\}) = e^{-\frac{t}{n}h_\perp^{(m)}}(\rho, \rho_1)\prod_{i=1}^{n-2}e^{-\tau_{i,n}\rho_i^2}e^{-\frac{t}{n}h_\perp^{(m)}}(\rho_i, \rho_{i+1})$$

$$\times e^{-\tau_{n-1,n}\rho_i^2}e^{-\frac{t}{n}h_\perp^{(m)}}(\rho_{n-1}, \rho')e^{-\tau_{n,n}\rho_i^2} \geqslant 0 \tag{35}$$

with $\tau_{i,n} = \tau_i + \tau_{n+i} + B^2/8$ embodies the degrees of freedom orthogonal to the internuclear axis. The 'parallel' function $G_t^{(\varepsilon,n)}$ in (34)

$$G_t^{(\varepsilon,n)}(\{\zeta\}, \{\tau\}) = \left(\frac{4\pi t}{n}\right)^{-n/2}\exp\left\{-\frac{n}{4t}\left((\zeta - \zeta_1)^2 + \sum_{i=1}^{n-2}(\zeta_i - \zeta_{i+1})^2 + (\zeta_{n-1} - \zeta')^2\right.\right.$$

$$\left.\left. - \sum_{i=1}^{n-1}\tau_i\zeta_i^2 - \tau_n(\zeta')^2 - \sum_{i=n+1}^{2n-1}\tau_i(\zeta_i - R)^2 - \tau_{2n}(\zeta' - R)^2\right)\right\} \tag{36}$$

can be integrated explicitly. The expression in (36) relevant for the integral over ζ_1 reads

$$\int d\zeta_1 \exp\left(-a(\zeta - \zeta_1)^2 - b(\zeta_1 - \zeta_2)^2 - c\zeta_1^2 - d(\zeta_1 - R)^2\right) = \sqrt{\frac{\pi}{S}}$$

$$\times \exp\left\{-S^{-1}\left(csR^2 + ad(\zeta - R)^2 + ac\zeta^2 + ab(\zeta - \zeta_2)^2\right.\right.$$

$$\left.\left. + bd(\zeta - R)^2 + bc\zeta_2^2\right)\right\}, \tag{37}$$

where $S = a + b + c + d$. Combining the right-hand side of (37) with the terms in (36) that contain ζ_2 leads to an integral over ζ_2 of the same form as on the left-hand side of (37) (with ζ_1 replaced by ζ_2, and ζ_2 by ζ_3, and where of course the coefficients a, b, c, d have changed). Therefore we can proceed successively to arrive eventually at

$$\int \prod_{i=1}^{n-1}d\zeta_i G_t^{(\varepsilon,n)}(\{\zeta\}, \{\tau\}) = c_0\exp\{-c_1R^2 - c_2(\zeta - R)^2 - c_3\zeta^2$$

$$- c_4(\zeta - \zeta')^2 - c_4(\zeta' - R)^2 - c_5(\zeta')^2\}, \tag{38}$$

with all $c_i > 0$ for $0 < \tau_j < \infty$. Since

$$e_m = \inf\sigma\left(h_{\text{cy}}^{(m)}\right) = -\lim_{t\to\infty}t^{-1}\ln K_t(\rho, \zeta, \rho', \zeta') \tag{39}$$

for any $\rho, \rho' \in \mathbb{R}^+$, $\zeta, \zeta' \in \mathbb{R}$, we now may choose, e.g., $\zeta = \zeta' = 0$, to see that the right-hand side of (38) is monotonically decreasing in R, which, together with (32), (34) proves the following theorem.

Theorem 5.2. *The lowest energies e_m within each angular momentum sector are monotonically increasing in the internuclear separation R, i.e., $e_m[R, B, Z_1, Z_2] \leqslant e_m[R', B, Z_1, Z_2]$ if $R \leqslant R'$.*

Moreover, by the same arguments an analogous result can be derived for multicentre systems with $\mathcal{C}_{\infty v}$ or $\mathcal{D}_{\infty h}$ symmetry. More precisely, if $v[R, Z_1, Z_2]$ in (5) is replaced by $v[\{R\}, \{Z\}] = -\sum_{k=1}^{N} Z_k / \sqrt{\rho^2 - (\zeta - R_k)^2}$, with $Z_k > 0, k = 1, \ldots, N$, then the corresponding N-centre electronic energies obey $e_m[\{R\}, B, \{Z\}] \leqslant e_m[\{R'\}, B, \{Z\}]$ if $|R_k - R_j| \leqslant |R'_k - R'_j|$ for all $1 \leqslant j < k = 2, \ldots, N$.

6. Consequences of the monotonicity

Given any electronic curve $e_m[R, B, Z_1, Z_2]$, one has to distinguish between the associated electronic binding energy $\mathrm{IP}_m[R, B, Z_1, Z_2]$ and the molecular binding energy $D_{e,m}[B, Z_1, Z_2]$. The former, namely, the ionization energy $\mathrm{IP}_m[R, B, Z_1, Z_2] = \inf \sigma_{\mathrm{ess}}\big(h_{\mathrm{cy}}^{(m)}[R, B, Z_1, Z_2]\big) - e_m[R, B, Z_1, Z_2]$ is determined by the distance to the threshold of the continuous spectrum, and, within the Born–Oppenheimer approximation, depends on R. As already mentioned in section 2, the potential operator v is $h_{\mathrm{mag}}^{(m)}[B]$-compact; thus we can infer the equality $\sigma_{\mathrm{ess}}\big(h_{\mathrm{cy}}^{(m)}[R, B, Z_1, Z_2]\big) = \sigma_{\mathrm{ess}}\big(h_{\mathrm{mag}}^{(m)}[B]\big)$ with $\inf \sigma_{\mathrm{ess}}\big(h_{\mathrm{mag}}^{(m)}[B]\big) = B/2$. Consequently, from theorem 5.1 and the preceding discussion the following behaviour of the ionization energies is obvious.

Corollary 6.1. *The ionization energy of the lowest state in each angular momentum sector decreases monotonically in R and also in the nuclear charge parameters Z_1, Z_2. It is bounded by the atomic ionization energies of the UAL and SAL, $\mathrm{IP}_m[\infty, B, Z_1, Z_2] \leqslant \mathrm{IP}_m[R, B, Z_1, Z_2] \leqslant \mathrm{IP}_m[0, B, Z_1, Z_2]$.*

The molecular binding energy, namely, the dissociation energy $D_{e,m}[B, Z_1, Z_2] = e[\infty, B, Z_1, Z_2] - E[R_e, B, Z_1, Z_2]$ measures the energy difference between the minimum of the PEC and its asymptotics in the SAL $R \to \infty$. That indeed $e[\infty, B, Z_1, Z_2]$ equals the hydrogenic energy is established in our next result.

Theorem 6.1. *Assume $Z_1 = \max\{Z_1, Z_2\}$; then in the SAL*

$$\lim_{R \to \infty} e_m[R, B, Z_1, Z_2] = e_m[0, B, Z_1, 0]. \tag{40}$$

To prove (40), let ϕ_m^{at} denote the (normed) lowest state wavefunction for the atomic operator $h_{\mathrm{cy}}^{(m)}[0, B, Z_1, 0]$. By the min–max principle

$$e_m[R, B, Z_1, Z_2] \leqslant e_m[0, B, Z_1, 0] - \left\langle \phi_m^{\mathrm{at}}, \frac{Z_2}{\sqrt{\rho^2 + (\zeta - R)^2}} \phi_m^{\mathrm{at}} \right\rangle \leqslant e_m[0, B, Z_1, 0] \tag{41}$$

and, due to the monotonic increase of $e_m[R, B, Z_1, Z_2]$, the limit $R \to \infty$ must exist. Now a variational test function for $h_{\mathrm{cy}}^{(m)}[0, B, Z_1, 0]$ is constructed with the help of the localization function $\chi \in C^1(\mathbb{R})$,

$$\chi_R(\zeta) := \begin{cases} 1 & \text{if } \zeta < R/4, \\ R^{-3}\zeta(3R - 4\zeta)^2 & \text{if } R/4 \leqslant \zeta \leqslant 3R/4, \\ 0 & \text{otherwise} \end{cases} \tag{42}$$

so that

$$e_m[0, B, Z_1, Z_2] \leqslant \left\langle \chi_R \phi_m, \left(h_{\text{cy}}^{(m)}[R, B, Z_1, Z_2] + \frac{Z_2}{\sqrt{\rho^2 + (\zeta - R)^2}} \right) \chi_R \phi_m \right\rangle \Big/ \|\chi_R \phi_m\|^2$$

(43)

where ϕ_m stands for the ground state of $h_{\text{cy}}^{(m)}[R, B, Z_1, Z_2]$. In equation (43) the expectation value for the Hamiltonian can be rewritten as $\left\langle \chi_R \phi_m, h_{\text{cy}}^{(m)}[R, B, Z_1, Z_2] \chi_R \phi_m \right\rangle = e_m[R, B, Z_1, Z_2]\|\chi_R \phi_m\|^2 + \|\chi_R' \phi_m\|^2 + 2\langle \phi_m, \chi_R \chi_R' \phi_m \rangle$, and, after computing $\chi_R' = \partial \chi_R / \partial \zeta$, we estimate $\|\chi_R' \phi_m\|^2 \leqslant 9R^{-2}\|\phi_m\|^2$ and $|\langle \phi_m, \chi_R \chi_R' \phi_m \rangle| \leqslant 3R^{-1}\langle \phi_m, \chi_R \phi_m \rangle$. Since for any fixed $R_0 > 0$ and all $R \geqslant R_0$ the norm $\|\chi_R \phi_m\|$ is uniformly bounded below by a strictly positive constant, the estimates above imply

$$\left\langle \chi_R \phi_m, h_{\text{cy}}^{(m)}[R, B, Z_1, Z_2] \chi_R \phi_m \right\rangle = e_m[R, B, Z_1, Z_2] + \text{O}(R^{-1}).$$

(44)

Similarly,

$$\left\langle \chi_R \phi_m, \frac{Z_2}{\sqrt{\rho^2 + (\zeta - R)^2}} \chi_R \phi_m \right\rangle \leqslant \sup_{\substack{0 < \rho < \infty \\ -\infty < \zeta \leqslant 3R/4}} \left\{ \frac{Z_2}{\sqrt{\rho^2 + (\zeta - R)^2}} \right\} \|\chi_R \phi_m\|^2$$

$$= 4R^{-1}\|\chi_R \phi_m\|^2,$$

(45)

whence $e_m[0, B, Z_1, 0] \leqslant e_m[R, B, Z_1, Z_2] + \text{O}(R^{-1})$ which, in combination with (41), proves the theorem.

Having identified the SAL, we can derive a simple lower bound on the position R_e of global minima of the PECs. The stability condition combined with the monotonicity of the electronic curves yields

$$e_m\big[R_{\text{LB}}^{(0)}, B, Z_1, Z_2\big] + \frac{Z_1 Z_2}{R_e} \leqslant E_m[R_e, B, Z_1, Z_2]$$

$$< e_m[\infty, B, Z_1, Z_2] = e_m[0, B, \max\{Z_1, Z_2\}, 0]$$

(46)

for any $0 \leqslant R_{\text{LB}}^{(0)} \leqslant R_e$, and thus leads to an improved lower bound $R_{\text{LB}}^{(1)}$ on R_e

$$R_e > R_{\text{LB}}^{(1)} = \frac{Z_1 Z_2}{e_m[0, B, \max\{Z_1, Z_2\}, 0] - e_m\big[R_{\text{LB}}^{(0)}, B, Z_1, Z_2\big]}.$$

(47)

An iteration ending up at

$$R_e \geqslant \lim_{n \to \infty} R_{\text{LB}}^{(n)} = \lim_{n \to \infty} \frac{Z_1 Z_2}{e_m[0, B, \max\{Z_1, Z_2\}, 0] - e_m\big[R_{\text{LB}}^{(n-1)}, B, Z_1, Z_2\big]}$$

(48)

appears possible in principle [25]; in practice, however, the energy values (or sufficiently sharp lower bounds) required at the $R_{\text{LB}}^{(n)}$ are difficult to calculate. Nonetheless, taking $R_{\text{LB}}^{(0)} = 0$, and focusing onto $m \geqslant 0$, for the first step

$$R_{\text{LB}}^{(1)} = \frac{Z_1 Z_2}{e_m[0, B, \max\{Z_1, Z_2\}, 0] - e_m[0, B, Z_1, Z_2]}$$

(49)

we can resort onto the known large B asymptotics for hydrogenic energies, e.g., from [12],

$$e_m[0, B, 1, 0] = \frac{B}{2} - \frac{1}{2}(\log(B))^2 + 2\log(B)\log(\log(B)) - 2(c_m + \log(2))\log(B)$$

$$- 2(\log(\log(B)))^2 + 4(c_m - 1 + \log(2))\log(\log(B)) + \text{O}(1)$$

(50)

where $C_m = -(\gamma_E + q_m)/2$, with $\gamma_E = 0.577\,215\,6649\ldots$ standing for the Euler constant, and q_m defined recursively by $q_0 = 0$, $q_m = q_{m-1} + 1/m$ if > 0. Restricting to leading

order in B and invoking the scaling relation (20), for homonuclear systems $Z = Z_1 = Z_2$ the denominator in (49) becomes

$$
e_m[0, B, Z, 0] - e_m[0, B, 2Z, 0] = Z^2 \left(\frac{3}{2} (\log(B))^2 - 2(3 \log(Z) + 4 \log(2)) \log(B) \right.
$$

$$
\left. + 2(3(\log(Z))^2 + 8 \log(2) \log(Z) + 4(\log(2))^2) \right) + O(\log(B) \log(\log(B)))
$$

$$
= \frac{3}{2} Z^2 (\log(B))^2 + O(\log(B) \log(\log(B))). \tag{51}
$$

The lower bound resulting from (51) is compatible with the behaviour $R_e \propto \frac{1}{2} (\log(B))^{-3/2}$ derived for the ground state $m = 0$ by approximating the system by a model with point (δ) interactions [8]. The numerical avail of theses large B expansions, however, is hampered by their slow convergence. For fields, e.g., $B = 10^4$, we obtain from (51) the lower bound 0.012 (or 0.029 if the expansion (50) is employed up to $O(\log(\log(B)))$) as compared to $R_{\mathrm{LB}}^{(1)} = 0.039$ from inserting computed hydrogenic energies e_0 [18]; the equilibrium separation extracted from variational [4] or finite elements [18] calculations is $R_e = 0.119$. For B as huge as 10^5 (and thus already beyond the domain of the nonrelativistic theory), we find lower bounds $R_{\mathrm{LB}}^{(1)}$ of 0.0072 (from (51)), 0.016 (from (50) up to $O(\log(\log(B)))$), or 0.022 (from numerical e_0 [18]), confirming that the expansions (50) and (51) are still far from being very accurate. On the other hand, it may be worth pointing out that the bounds emerging from (51) hold for all m and not only for the ground state $m = 0$. Also (51) is not just an upper bound on the dissociation energy D_e, but describes precisely the leading order of D_e for the ground state (cf equation (15) in [8]).

7. Decay of eigenfunctions

Decay properties of eigenfunctions have been established for a large class of Schrödinger operators; in particular, it is well known that atomic or molecular bound state wavefunctions decrease exponentially (pointwise and in L^2 sense) for distances sufficiently far away from the nuclear centres [22, 20]. Apparently, however, this behaviour is less intensely studied for systems in a magnetic field. Since in the presence of a field nonisotropic effects can be expected, the Agmon method [20] is certainly best suited for controlling the decay behaviour. Below, adapting standard arguments of this technique, we demonstrate that, for $\mathbf{B} \neq 0$, in the direction transversal to the $\mathbf{B}$ field the two-centre bound state wavefunctions decay even faster, viz, decrease like Gaussians and the lowest Landau orbital $\exp(-B\rho^2/4)$. An analogous result for atoms was derived by Avron, Herbst and Simon [12]; their proof employs stochastic ingredients (i.e., the Feynman–Kac formula).

Theorem 7.1. *Let $\psi_{m,k}$ be an eigenfunction (not necessarily the ground state) of $h_{\mathrm{cy}}^{(m)}$ with eigenvalue $e_{m,k}$. Considering a nonvanishing field $B \neq 0$ and taking $\delta > 0$, we set*

$$
\rho_0 = 2B^{-2} \left(\delta + e_{m,k} + \sqrt{(\delta + e_{m,k})^2 + (Z_1 + Z_2)B^2} \right) \tag{52}
$$

and define an 'Agmon metric' by

$$
d_{m,k} = \max \left\{ 0, \int_{\rho_0}^{\rho} \sqrt{2(B^2 s^2/8 - (Z_1 + Z_2)/s - e_{m,k})} \, \mathrm{d}s \right\}. \tag{53}
$$

Then for any $\varepsilon > 0$ there exist a constant $0 < c_\varepsilon < \infty$ such that

$$
\| \mathrm{e}^{(1-\varepsilon)d_{m,k}} \psi_{m,k} \| \leqslant c_\varepsilon. \tag{54}
$$

*The bound (54) implies that in the direction orthogonal to the **B** field all bound state wavefunctions decay like a Gaussian, where in leading order the exponent is determined by $(1 - \varepsilon)B\rho^2/4$ in the sense $\psi_{m,k} \in \mathcal{D}(\exp((1 - \varepsilon)B\rho^2/4))$ for all $\varepsilon > 0$.*

To prove (54), we first note that the choice (52) implies $v_{m,k} := B^2\rho^2/8 - (Z_1 + Z_2)/\rho - e_{m,k} \geqslant \delta$ for $\rho \geqslant \rho_0$; thus $d_{m,k}$ in (53) is well defined. Denoting $F_\varepsilon(\rho) := (1 - \varepsilon)d_{m,k}$ we obtain for any ϕ in the domain of $h_{\text{cy}}^{(m)}$ with supp $\phi \subset [\rho_0, \infty)$

$$\text{Re}\langle e^{F_\varepsilon}\phi, (h_{\text{cy}}^{(m)} - e_{m,k}) e^{-F_\varepsilon}\phi\rangle = \text{Re}\left\langle \phi, \left(h_{\text{cy}}^{(m)} - e_{m,k} - \frac{1}{2}\left(\frac{\partial F_\varepsilon}{\partial\rho}\right)^2\right)\phi\right\rangle$$
$$\geqslant \text{Re}\langle\phi, \varepsilon v_{m,k}\phi\rangle \geqslant \varepsilon\delta\|\phi\|^2. \tag{55}$$

The equality in the top line of (55) holds because the expectation value of the sum of the remaining derivatives of F_ε has no nonvanishing real part. Furthermore, in (52) we used the estimate $-(\partial F_\varepsilon/\partial\rho)^2 \geqslant -2(1 - \varepsilon)v_{m,k}$ for $\rho \geqslant \rho_0$, the positivity of the kinetic energy, and bounds like $-1/\sqrt{\rho^2 + \zeta^2} \geqslant -1/\rho$ on the Coulomb terms. Next, we construct a twice differentiable function χ by

$$\chi(\rho) := \begin{cases} 0 & \text{if} \quad 0 < \rho < \rho_0, \\ 3(\rho - \rho_0)^2 - 2(\rho - \rho_0)^3 & \text{if} \quad \rho_0 \leqslant \rho \leqslant \rho_0 + 1, \\ 1 & \text{if} \quad \rho > \rho_0 + 1 \end{cases} \tag{56}$$

so that $\partial\chi/\partial\rho$ and $\partial^2\chi/\partial\rho^2$ vanish if $\rho \notin (\rho_0, \rho_0 + 1)$, while for $\rho_0 < \rho < \rho_0 + 1$

$$\left|\frac{\partial\chi}{\partial\rho}\right| \leqslant \frac{3}{2} \qquad \text{and} \qquad \left|\frac{\partial^2\chi}{\partial\rho^2} + \rho^{-1}\frac{\partial\chi}{\partial\rho}\right| \leqslant 6. \tag{57}$$

Choosing $\phi = e^{F_\varepsilon}\chi\psi_{m,k}$, inequality (55) is recast into

$$\text{Re}\langle e^{2F_\varepsilon}\chi\psi_{m,k}, (h_{\text{cy}}^{(m)} - e_{m,k})\chi\psi_{m,k}\rangle \geqslant \varepsilon\delta\|e^{F_\varepsilon}\chi\psi_{m,k}\|^2. \tag{58}$$

To derive an upper bound on the left-hand side of (58), we calculate

$$\left|\langle e^{2F_\varepsilon}\chi\psi_{m,k}, (h_{\text{cy}}^{(m)} - e_{m,k})\chi\psi_{m,k}\rangle\right|$$
$$= \left|\left\langle e^{2F_\varepsilon}\chi\psi_{m,k}, \left(-\frac{1}{2\rho}\left(\frac{\partial}{\partial\rho}\rho\frac{\partial\chi}{\partial\rho}\right) - \left(\frac{\partial\chi}{\partial\rho}\right)\frac{\partial}{\partial\rho}\right)\psi_{m,k}\right\rangle\right|$$
$$\leqslant \frac{1}{2}\left|\left\langle e^{2F_\varepsilon}\chi\psi_{m,k}, \left|\frac{1}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial\chi}{\partial\rho}\right|\psi_{m,k}\right\rangle\right| + \left|\left\langle e^{2F_\varepsilon}\chi\psi_{m,k}, \frac{\partial\chi}{\partial\rho}\frac{\partial}{\partial\rho}\psi_{m,k}\right\rangle\right| \tag{59}$$

and, with the help of (57) and $\sup_{\rho_0\leqslant\rho\leqslant\rho_0+1}\{F_\varepsilon(\rho)\} = F_\varepsilon(\rho_0 + 1)$, we estimate

$$\left|\left\langle e^{2F_\varepsilon}\chi\psi_{m,k}, \left|\frac{1}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial\chi}{\partial\rho}\right|\psi_{m,k}\right\rangle\right| \leqslant 6\, e^{2F_\varepsilon(\rho_0+1)}\|\psi_{m,k}\|^2 \tag{60}$$

and

$$\left|\left\langle e^{2F_\varepsilon}\chi\psi_{m,k}, \frac{\partial\chi}{\partial\rho}\frac{\partial}{\partial\rho}\psi_{m,k}\right\rangle\right| \leqslant \frac{3}{2}\, e^{2F_\varepsilon(\rho_0+1)}\|\psi_{m,k}\|\left\|\frac{\partial}{\partial\rho}\psi_{m,k}\right\|. \tag{61}$$

Taking a sufficiently large $\lambda > 0$ in the resolvent set of $h_{\text{cy}}^{(m)}$, the last factor in (61) is bounded by

$$\left\|\frac{\partial}{\partial\rho}\psi_{m,k}\right\| \leqslant \left\|\frac{\partial}{\partial\rho}(h_{\text{cy}}^{(m)} + \lambda)^{-1}\right\|\|(e_{m,k} + \lambda)\psi_{m,k}\| = |e_{m,k} + \lambda|\left\|\frac{\partial}{\partial\rho}(h_{\text{cy}}^{(m)} + \lambda)^{-1}\right\|\|\psi_{m,k}\|. \tag{62}$$

Hence, assuming that $\psi_{m,k}$ is normed to one, upon combining (59)–(62) we arrive at

$$\varepsilon\delta\|e^{F_\varepsilon}\chi\psi_{m,k}\| \leqslant \text{const}\, e^{2F_\varepsilon(\rho_0+1)}, \tag{63}$$

where the constant depends on ε and δ and on the respective energy and state. Inequality (54) now follows from straightforward estimates. Moreover, since for $s \geqslant \rho_0$ in the Agmon metric $v_{m,k}(s) \geqslant B^2 \rho^2/8 - (Z_1 + Z_2)/\rho_0 - e_{m,k}$, integration of the latter yields

$$\int_{\rho_0}^{\rho} v_{m,k}(s)\,\mathrm{d}s \geqslant \frac{B\rho^2}{4}\sqrt{1 - \frac{8a_{m,k}}{B^2\rho^2}} - a_{m,k}B^{-1}\log\left(4\sqrt{2}B\rho + 16\sqrt{\frac{B^2\rho^2}{8} - a_{m,k}}\right) + d_0, \quad (64)$$

where $a_{m,k} = \rho_0^{-1}(Z_1 + Z_2) - e_{m,k}$ and d_0 contains the constant contributions from the lower integration boundary. This leads to the leading term of the decay as stated in the theorem.

Physically, along the magnetic field, there is no reason for a similar strong decay of the wavefunctions; rather, the $\psi_{m,k}$ can be expected to show the same type of exponential behaviour as for vanishing field. Since for large B the energies $e_{m,k}$ become positive and thus longitudinal classical motion unbounded, the Agmon approach does not allow to deduce the quantum decay in the ζ variable. On the other hand, Avron *et al* [12] remark that such 'normal' decay properties follow easily from the standard Combes–Thomas method [19]. This remains true for molecular systems, whence here we merely outline the main arguments. Starting with the unitary group

$$U_{\|}(\lambda)\psi_{m,k} = \mathrm{e}^{\mathrm{i}\lambda\zeta}\psi_{m,k} \tag{65}$$

for $\lambda \in \mathbb{R}$, in the correspondingly transformed Hamiltonian

$$h_{\mathrm{cy}}^{(m)}(\lambda) := U_{\|}(\lambda)h_{\mathrm{cy}}^{(m)}U_{\|}(\lambda)^{-1} \tag{66}$$

only the ζ-part of the kinetic is changing, namely, into $(-\mathrm{i}\partial/\partial\zeta - \lambda)^2/2$. Thus, obviously, by (66) an analytic family (of type A) is defined. Setting $R_{m,k} = \{\lambda \in \mathbb{C} \,|\, |\mathrm{Im}\,\lambda| < \sqrt{B - 2e_{m,k}}\}$ and using that $e_{m,k} \notin \sigma_{\mathrm{ess}}\big(h_{\mathrm{cy}}^{(m)}(\lambda)\big)$ if $\lambda \in R_{m,k}$, the analyticity of $h_{\mathrm{cy}}^{(m)}(\lambda)$ implies the existence of projections $P(\lambda)$, analytic for $\lambda \in R_{m,k}$, such that $\dim(\mathrm{Ran}\,P(\lambda)) < \infty$ where the range $\mathrm{Ran}\,P(\lambda)$ of $P(\lambda)$ is spanned by the eigenvectors of $h_{\mathrm{cy}}^{(m)}(\lambda)$ associated with the eigenvalue $e_{m,k}(\lambda)$. Moreover, $P(\lambda)$ obeys $U_{\|}(\lambda')P(\lambda)U_{\|}(\lambda')^{-1} = P(\lambda + \lambda')$ for $\lambda \in R_{m,k}$ (including $\lambda = 0$) and all $\lambda' \in \mathbb{R}$. Hence, the prerequisites for O'Connor's lemma (see, e.g., p 196 in [22], or [26]) are met, and we infer that $\psi_{m,k}$ is an analytic vector for the position operator ζ, i.e., $\exp(\mathrm{i}\lambda\zeta)\psi_{m,k}$ is analytic in λ for $\lambda \in R_{m,k}$, and the following theorem results.

Theorem 7.2. *The eigenfunctions $\psi_{m,k}$ of $h_{\mathrm{cy}}^{(m)}$ with eigenvalue $e_{m,k}$ decay exponentially in ζ-direction, $\psi_{m,k} \in \mathcal{D}(\mathrm{e}^{(1-\varepsilon)\sqrt{B-2e_{m,k}}|\zeta|})$ for all $\varepsilon > 0$.*

Whereas the transversal exponent $B\rho^2/4$ in theorem 7.1 is certainly optimal, the exponent $\sqrt{B - 2e_{m,k}}$ of theorem 7.2 probably can be improved. Furthermore, given the decay in L^2-sense proved in these theorems, pointwise decay can be deduced by conventional regularity (namely, C^∞ away from the nuclear centres) properties of the wavefunctions.

8. Concluding remarks

In the preceding sections, by means of standard mathematical techniques, we deduced several results for the one-electron two-centre system. If the respective property is not specific to the presence of only a single electron, such as the positivity of the wavefunctions ϕ_m considered in section 2, an extension to diatomic molecules with $N > 1$ electrons may be possible, although not always straightforward. On the other hand, already for the one-electron system there remain enough interesting problems still unsettled, even if attention is restricted to systems

within the Born–Oppenheimer approximation and the nonrelativistic regime (for problems arising in a relativistic treatment, see, e.g. [28]).

From a practical point of view, a major progress would be the rigorous confirmation of the numerical observation [4] that the ground state energy of $H[\mathbf{R}, \mathbf{B}, Z_1, Z_2]$ attains its minimum for parallel configurations, i.e., for $\mathbf{R} \wedge \mathbf{B} = 0$. This also would justify that here—like in most other theoretical studies—the focus has been on situations where the magnetic field and the internuclear axis are parallel. Concerning extensions to nonparallel configurations, whereas—at least for sufficiently large $r_\perp$—the decay of bound state wavefunctions in directions orthogonal to $\mathbf{B}$ is certainly Gaussian with exponent $Br_\perp/4$, it is not clear whether the electronic energies still behave monotonically as a function of the nuclear separation. Monotonicity in R is definitely not a universal property of the electronic curves; since for $B = 0$ most of the excited states exhibit nonmonotonic curves, this probably will be also the case if $B \neq 0$. Monotonicity of binding energies in B is a question not examined in our study; for the hydrogen atom, Avron *et al* [12] proved that the ionization energy increases monotonically with B. A similar behaviour can be expected for the ionization and dissociation energies of the one-electron molecular system, with both energies asymptotically growing as $(\log B)^2$.

Besides those applications discussed in section 6, monotonicity properties play a role in binding and stability problems [3, 27]. In the same context, the molecular virial theorem enters into the argumentation, so that now, with these items generalized to $B \neq 0$, they are at disposal for investigating stability in magnetic fields. Furthermore, in numerical calculations the virial theorem serves as a valuable tool to asset the accuracy of the computations [18]. Finally, the monotonicity of the energy levels in the angular momentum quantum number m demonstrated in section 4 gives a rigorous justification of the common assumption (also employed, e.g., in [7]) that $m = 0$ provides the ground state of the system.

Acknowledgment

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