Two-centre Dirac-Coulomb operators: Regularity and bonding properties

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Assuming the Born-Oppenheimer (clamped nuclei) approximation, basic properties of the Dirac operator for homonuclear two-centre one-electron systems are studied. This includes a rigorous analysis of the regularity of the potential energy curves as a function of the internuclear distance; in particular, for all values of the nuclear charge parameter that guarantee existence of a physically reasonable self-adjoint extension of the corresponding atomic Dirac-Coulomb operator, the continuity and differentiability of the electronic contribution to the potential energy curves are shown also to hold in the united atom limit. Furthermore, for nuclear charges not too large, the ground state united atom energy is demonstrated to provide a universal lower bound to all molecular energies within the discrete spectrum. Together with a generalization of the virial theorem to diatomic Dirac-Coulomb operators, this leads to a lower bound on the equilibrium separation between the nuclei. In addition, by employing appropriate variational arguments, the possibility of molecular bonding (for sufficiently large nuclear mass) is proved for all systems with charges up to those of the hydrogen molecular ion H_2^+.

1. INTRODUCTION

Within atomic theory, the nonrelativistic as well as the relativistic quantum models of the hydrogen atom enjoy fundamental impact. One of the reasons for their importance is that the presence of only a single electron allows for explicit solutions to the corresponding Schrödinger and Dirac equation (see, e.g., Messiah [1]). A similar prominent role for the understanding of molecular bonding is played by the hydrogen molecule ion H_2^+ ([2, 3]). For the molecular system, however, the situation is less explicit. Assuming the nuclei fixed and a nonrelativistic kinematics for the motion of the electron within the Coulomb potential of both nuclear centres, the

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Schrödinger equation can be separated by changing to prolate spheroidal coordinates [4]; unfortunately, after separation there remains a coupled Sturm-Liouville system of two ordinary differential operators that – apart from very exceptional ratios of the nuclear charges and internuclear separations [5] – cannot be solved by elementary functions. Even worse, when treating the electron relativistically, the two-centre Dirac equation apparently cannot be separated to the same extend as in the Schrödinger case [6, 7, 8]. Hence, alternative methods are required to derive qualitative and quantitative information on the relativistic one-electron two-centre system.

The current status of relativistic many-body theory for atoms and molecules is controversial to some extend [9, 10]. Nonetheless, despite of several not yet completely settled fundamental questions, numerical investigations of atoms employing various quantum chemical techniques and diverse versions of relativistic multi-electron Hamiltonians are nowadays almost considered as routine work [11, 12]. For molecules, too, such calculations are increasingly becoming feasible [13]. Also for the description of quasi-molecular states in heavy ion collisions, the two-centre Dirac equation has received – and continues to attract – considerable attention (see [7, 8, 14, 15, 16, 17, 18] and references therein). In the molecular situation, independently of how the two-body part, viz., the electron-electron interaction is implemented, the one-body part of the Hamiltonian usually consists of a sum of two- (or multi-)centre one-electron Dirac-Coulomb operators. Hence, serving as basic constituents of relativistic molecular theory, such Dirac-Coulomb operators certainly deserve a careful and detailed examination.

Here, our aim is to analyze several intrinsic spectral properties of the Dirac-Coulomb Hamiltonian in a mathematically rigorous way. Throughout our study we regard the nuclei as being "clamped"; thus, the nuclear separation vector is taken as a parameter for the Hamiltonian and its spectrum. First, we try to elucidate the smoothness of the Dirac-Coulomb energies as a function of the internuclear separation, i.e., the behaviour of the "potential energy curves (PECs)" (if nuclear repulsion is included) or the "electronic curves" (without nuclear repulsion). Due to the peculiar break in self-adjointness innate to the Dirac-Coulomb operator for growing nuclear charge parameters, the limiting situation of coalescing nuclear centres may be anticipated as a touchy point for electronic curves; behind, of course, is the "artificial" modeling of the nuclei as point particles, and the arising problems could be alleviated if the nuclei were replaced by extended "smeared-out" charge distributions. Nevertheless, even in the singular setup, the electronic curves can be proved to retain some regularity if the internuclear distance shrinks to zero. Our result on this problem extends previous findings by Klaus [19]; the crucial modification in the proof consists in the way how zero-energy molecular eigenvalues are excluded. Also to this end it is of profound interest to estimate the molecular energies from below by the ground state energy of the "united atom". Strikingly, such a lower bound requires significantly more sophisticated arguments than the analogous bound for Schrödinger energies, and we are merely able to prove it for nuclear charges that do not exceed a certain maximal value.

With the sufficient smoothness of the electronic curves established, we can keep to beaten paths to formulate and demonstrate a Feynman-Hellman theorem for the derivatives with respect to the nuclear separation. Less customary is the generalization of the relativistic virial theorem from atomic to molecular systems. In particular, and unlike to the Schrödinger case, for the molecular Dirac-Coulomb Hamiltonian the virial theorem can also be expressed in an integrated version. Furthermore, employing the virial theorem and the lower bound on the molecular energies, the equilibrium size of the molecule can be estimated from below.

The question whether atoms are capable to form molecular bonds by sharing electrons lies at the heart of quantum chemistry. Since the hydrogen molecule ion H_2^+ represents the simplest multi-centre system and therefore furnishes the easiest possibility for investigations, its nonrelativistic model is discussed under these aspects in numerous textbooks (see, e.g., [20, 21, 22]). Usually, bonding of H_2^+ is proved by the LCAO method. That is, a linear combination of (appropriately translated) atomic orbitals serves as a test function to calculate variational upper energy bounds; then, it is verified that there are (finite) internuclear separations for which these bounds are smaller than the known hydrogenic energy for the asymptotic configuration of infinitely apart nuclei .

A literal transcription of the above procedure to relativistic H_2^+ is hampered by the fact that the Coulomb-Dirac Hamiltonian is not semibounded from below (or, from above, either). Thus, the conventional Rayleigh-Ritz variational principle cannot be applied. Moreover, despite of recent progress in variational characterizations of Dirac eigenvalues [23, 24, 25], unfortunately these rigorous minimax theorems do not lead to upper bounds along the same straightforward lines as for Schrödinger operators. Due to these difficulties and the nonseparability of the two-centre Dirac-Coulomb Hamiltonian, apparently a rigorous demonstration of bonding properties had not yet been accomplished for relativistic molecules. Here, the stratagem we are resorting to is to consider the square of the Dirac-Coulomb Hamiltonian. This operator is clearly nonnegative; so, we can fall back onto the standard minimax principle and the LCAO upper bound. On the other hand, even for the very simple ansatz of the test function as an atomic ground state attached to merely one nuclear centre, the arising integrals cannot be computed in closed form. Nonetheless, by determining asymptotic expressions for these integrals or by estimating certain LCAO integrals we are able to save the approach and to deduce chemical bonding for the relativistic two-centre one-electron system.

Below, in chapter 2, we start our exposition by recalling the precise definition and the self-adjointness behaviour of the studied Dirac-Coulomb operators. Since also symmetry and scaling arguments enter into our analysis, they are explained in section 2.2. Known results about the limit of infinite internuclear separation are outlined in section 2.3, and the lower bound on molecular energies in terms for the "united atom" energy is established in section 2.4. We show the regularity of the electronic curves in chapter 3; first, in section 3.1, the continuity, then, in section 3.2, differentiablity; in section 3.3 we prove the Feynman-Hellman theorem . The relativistic virial theorem (section 4.1) and our discussion of bonding are presented in chapter 4. In appendix A we collect a few recent results about variational methods for Dirac eigenvalues, and in appendix B we display the matrix elements that are needed for our stability proof. Finally, chapter 5 is devoted to concluding remarks and to an outlook.

2. THE TWO-CENTRE DIRAC-COULOMB OPERATOR

We study one-electron systems for which the electronic states are identified with vectors in the Hilbert space

$$\mathcal{H} = L^2(\mathbb{R}^3, \mathbb{C}^4) \cong L^2(\mathbb{R}^3, \mathbb{C}) \otimes \mathbb{C}^4 \tag{2.1}$$

equipped with the inner product

$$\langle \psi,\, \phi \rangle = \int \sum_{i=1}^{4} \overline{\psi_i}(x)\phi_i(x)\, d^3x \tag{2.2}$$

for $\psi, \phi \in \mathcal{H}$. The clamped nuclei (or BO) approximation means that the two nuclear centres are fixed at positions $+\frac{1}{2}\boldsymbol{R}$ and $-\frac{1}{2}\boldsymbol{R}$, respectively, and the electronic quantities are regarded as function of the internuclear separation $\boldsymbol{R} \in \mathbb{R}^3$. Here, we focus onto homonuclear systems, viz., identical charges $+Ze_0$ for both nuclei. In this context, it will be convenient to choose the mass m_e of the electron as new mass unit, and the Compton wavelength of the electron $\lambda_e = \hbar/m_e c$ as the length unit. Furthermore, denoting the Sommerfeld fine structure constant by $\alpha_S = e_0^2/\hbar c$, we take $\zeta := \alpha_S Z$ as the nuclear charge parameter. Then, an appropriate scaling of the length variables casts the free Dirac operator into the form:

$$T_D = \boldsymbol{\alpha} \cdot \boldsymbol{p} + \beta. \tag{2.3}$$

Here, $\boldsymbol{p} = -i\boldsymbol{\nabla}$, and the standard Dirac matrices $\alpha_1, \alpha_2, \alpha_3, \beta$ are given in terms of the Pauli matrices or the 2×2 unit matrix $\mathbb{I}_2$ by

$$\alpha_j = \begin{pmatrix} 0 & \sigma_j \\ \sigma_j & 0 \end{pmatrix}, \qquad \beta = \begin{pmatrix} \mathbb{I}_2 & 0 \\ 0 & -\mathbb{I}_2 \end{pmatrix}. \tag{2.4}$$

The molecular Hamiltonian contains T_D as its kinetic energy part, and a potential V that depends parametrically on $\boldsymbol{R}$ and ζ:

$$H(\boldsymbol{R}, \zeta) = T_D + V(\boldsymbol{R}, \zeta). \tag{2.5}$$

In V, we distinguish between different contributions,

$$V(\boldsymbol{R}, \zeta) = V_{\mathrm{ne}}(\boldsymbol{R}, \zeta) + V_{\mathrm{nn}}(\boldsymbol{R}, \zeta), \tag{2.6}$$

where the nuclei-electron interactions

$$(V_{\mathrm{ne}}(\boldsymbol{R}, \zeta)\psi)(\boldsymbol{x}) = V_{\mathrm{ne}}(\boldsymbol{x};\, \boldsymbol{R}, \zeta)) \otimes \mathbb{I}_4\, \psi(\boldsymbol{x}) \tag{2.7}$$

is determined by the function

$$V_{\mathrm{ne}}(\boldsymbol{x};\, \boldsymbol{R}, \zeta)) = -\zeta(|\boldsymbol{x} - \tfrac{1}{2}\boldsymbol{R}|^{-1} + |\boldsymbol{x} + \tfrac{1}{2}\boldsymbol{R}|^{-1}), \tag{2.8}$$

whereas the nucleus-nucleus term acts simply as

$$(V_{\mathrm{nn}}(\boldsymbol{R}, \zeta)\psi)(\boldsymbol{x}) = V_{\mathrm{nn}}(\boldsymbol{R}, \zeta) \otimes \mathbb{I}_4\, \psi(\boldsymbol{x}) = \alpha_S^{-1}\zeta^2|\boldsymbol{R}|^{-1} \otimes \mathbb{I}_4\, \psi(\boldsymbol{x}). \tag{2.9}$$

For any given vector $\boldsymbol{x}$, by translating and rotating $\boldsymbol{x}$, one can find $\boldsymbol{x}_{\boldsymbol{R}}$ such that the nuclei-electron potential function has the same value as for the nuclei placed along a "standard" direction, i.e., at $\pm\boldsymbol{R}_s = (0, 0, \pm\frac{1}{2}R)$ on the z-axis,

$$V_{\mathrm{ne}}(\boldsymbol{x};\, \boldsymbol{R}, \zeta)) = V_{\mathrm{ne}}(\boldsymbol{x}_{\boldsymbol{R}};\, \boldsymbol{R}_s, \zeta)). \tag{2.10}$$

Implementing the transformation $\boldsymbol{x} \mapsto \boldsymbol{x}_{\boldsymbol{R}}$ by the unitary operator U_s on $\mathcal{H}$, then the invariance of the kinetic energy T_D under U_s together with Eq. (2.10) imply the unitary equivalence

$$H(\boldsymbol{R}, \zeta) = U_s H(\boldsymbol{R}_s, \zeta) U_s^{-1}. \tag{2.11}$$

Therefore, for a spectral analysis it is sufficient merely to study the dependence of H on the modulus R of $\boldsymbol{R}$. In the sequel, we will always assume the nuclei located at the z-axis symmetrically around the origin, and continue to (ab)use the same symbols for the operators, that is, $V(R, \zeta) := V(\boldsymbol{R}_s, \zeta)$, and similarly for $H(R,\zeta)$, $V_{\rm ne}(R,\zeta)$ and $V_{\rm nn}(R,\zeta)$. The nontrivial part of H is called the "electronic Hamiltonian" and denoted by

$$h(R,\zeta) = T_D + V_{\rm ne}(R,\zeta) \tag{2.12}$$

Two particular cases deserve to be singled out, namely the "united atoms limit" (UAL)

$$\lim_{R\downarrow 0} h(R,\zeta), \tag{2.13}$$

and the "separated atoms limit" (SAL)

$$\lim_{R\to\infty} h(R,\zeta). \tag{2.14}$$

Formally, one would expect the UAL being described by an atomic hydrogenic Hamiltonian for twice the nuclear charge, viz., by

$$h(0,\zeta) = T_D - 2\zeta|\boldsymbol{x}|^{-1}, \tag{2.15}$$

whereas the SAL would be governed by the hydrogen operator with charge ζ,

$$h(\infty,\zeta) = T_D - \zeta|\boldsymbol{x}|^{-1}. \tag{2.16}$$

Precise results for both limits will be discussed below.

2.1. Self-adjointness properties

To examine domain and self-adjointness questions for $h(R,\zeta)$, we have to distinguish between the situations $R=0$ and $R>0$. This is in sharp contrast to analogous one-electron Schrödinger operators, and related to the existence of a critical charge separating different self-adjointness regimes for the Dirac-Coulomb Hamiltonian. As a heuristic explanation we note that apparently the (relative) contribution of the kinetic energy T_D is less than the Schrödinger kinetic energy contribution $T_S = \boldsymbol{p}^2/2$ (containing the square of the momentum), so that for Dirac systems the electron could collapse within a finite time into the (pointlike) nucleus if the attractive potential gets too strong for large enough nuclear charge.

To construct systematically the molecular Hamiltonian, we first consider the kinetic part T_D; straightforward extension of arguments from Ref. [26] shows that T_D is essentially self-adjoint on $C_0^\infty(\mathbb{R}^3\setminus K_c)$ where K_c denotes a finite set of points in $\mathbb{R}^3$, e.g., $K_c=\{0\}$, or $K_c=\{-\frac{1}{2}\boldsymbol{R}_s, \frac{1}{2}\boldsymbol{R}_s\}$. Furthermore, T_D is self-adjoint on the Sobolev space $\mathcal{D}(T_D) = H^1(\mathbb{R}^3,\mathbb{C}^4)$, and has a purely absolutely continuous spectrum $\sigma(T_D)=\sigma_{\rm ac}(T_D)=\mathbb{R}\setminus(-1,+1)$ with the gap $(-1,1)$. Since $|\boldsymbol{x}\pm\frac{1}{2}\boldsymbol{R}_s|^{-1}$ is relatively bounded with respect to T_D with relative bound 2, one can invoke the Kato-Rellich theorem to arrive at a self-adjoint molecular Hamiltonian as long as the nuclear charge parameter obeys $2|\zeta| < 1/2$ if $R = 0$, or $|\zeta| < 1/2$ if $R > 0$. For the one-centre (atomic) operator

$$h_{\mathrm{at}}(\zeta) = T_D + V_{\mathrm{ne}}(0, \tfrac{1}{2}\zeta) \tag{2.17}$$

and more general $\zeta \geq 0$, the self-adjointness properties of h_{at} are summarized by:

THEOREM 2.1. *(i) If $2\,\zeta < \sqrt{3}/2$, then $h_{\mathrm{at}}(2\zeta)$ is essentially self-adjoint on $C_0^\infty(\mathbb{R}^3 \setminus \{0\}, \mathbb{C}^4)$, and self-adjoint on $H^1(\mathbb{R}^3, \mathbb{C}^4)$.*

(ii) If $\sqrt{3}/2 \leq 2\,\zeta < 1$, then $h_{\mathrm{at}}(2\zeta)$ is not essentially self-adjoint on $C_0^\infty(\mathbb{R}^3 \setminus \{0\}, \mathbb{C}^4)$. There exists, however, a unique self-adjoint extension that is characterized by finiteness of the kinetic energy, i.e., by $\mathcal{D}(h_{\mathrm{at}}(2\zeta)) \subset \mathcal{D}(|T_D|^{1/2})$, or, alternatively (and equivalently), by finiteness of the potential energy, $\mathcal{D}(h_{\mathrm{at}}(2\zeta)) \subset \mathcal{D}(\sqrt{2\,\zeta|\boldsymbol{x}|^{-1}})$.

The proofs for the assertions of theorem (2.1) are distributed among several articles in the literature; see, e.g. [27, 28, 29] for (i), or [27, 30, 31, 32, 33, 34] in case of (ii). For multicentre systems (also with more than two nuclei), corresponding self-adjointness results were demonstrated by Klaus [19]:

THEOREM 2.2. *Suppose $R > 0$.*

(i) If $|\zeta| < \sqrt{3}/2$, then $h(R,\zeta)$ is self-adjoint on the domain $\mathcal{D}(h(R,\zeta)) = \mathcal{D}(T_D) = H^1(\mathbb{R}^3, \mathbb{C}^4)$. This implies, in particular, that $h(R,\zeta)$ is essentially self-adjoint on any core for T_D, like, e.g., $\mathcal{D}_0 = C_0^\infty(\mathbb{R}^3 \setminus \{-\frac{1}{2}\boldsymbol{R}_s, \frac{1}{2}\boldsymbol{R}_s\}, \mathbb{C}^4)$.

(ii) For $\sqrt{3}/2 < |\zeta| < 1$, there exists a self-adjoint extension of $h_0(R,\zeta) := h(R,\zeta)_{\restriction \mathcal{D}_0}$ that is uniquely determined by $\mathcal{D}(h(R,\zeta)) \subset \mathcal{D}(|T_D|^{1/2})$, or, equivalently, by $\mathcal{D}(h(R,\zeta)) \subset \mathcal{D}(|V_{\mathrm{ne}}(R,\zeta)|^{1/2})$.

(iii) For all $|\zeta| < 1$ and the self-adjoint operators $h(R,\zeta)$ listed in (i) or (ii), the essential spectrum is independent of ζ and R, $\sigma_{\mathrm{ess}}(h(R,\zeta)) = \sigma_{\mathrm{ess}}(T_D) = \mathbb{R} \setminus (-1, +1)$

2.2. Symmetries and scaling

Since some symmetry properties of $h(R,\zeta)$ will be of relevance for our investigations, let us briefly recall that the symmetry transformations of a homonuclear diatomic molecule form the group $\boldsymbol{D}_{\infty h}$ (see, e.g., [35]). We can express $\boldsymbol{D}_{\infty h} = \boldsymbol{C}_{\infty h} \times \boldsymbol{C}_i$ as the product of its subgroups $\boldsymbol{C}_i$ and $\boldsymbol{C}_{\infty h}$. In addition to the group identity E, the latter contains the following symmetry operations: $\boldsymbol{C}_{\infty h} = \{E, C_\infty^\phi, \sigma_v \mid \phi \in (0, 2\pi)\}$; here, C_∞^ϕ denotes the rotation of angle ϕ around the internuclear axis, and σ_v the reflection at a vertical plane through the internuclear axis. The (sub)group $\boldsymbol{C}_i = \{E, i_O\}$ has as only nontrivial element the inversion transformation i_O at the origin O (= midpoint between the nuclear centres). Given these symmetry operations, the associated unitary transformations on $\mathcal{H}$ lead to unitary representations of the (discrete) group $\boldsymbol{C}_i$ or the (Lie) group $\boldsymbol{C}_{\infty h}$. If P_{i_O} stands for the operator $(P_{i_O} \otimes \mathbb{I}_4\psi)(\boldsymbol{x}) = \psi(i_O\boldsymbol{x})$, then the unitary transformation on $\mathcal{H}$ corresponding to the inversion operation i_O is the parity operator

$$P_O = P_{i_O} \otimes \beta. \tag{2.18}$$

In the same way, defining

$$\Sigma_i = \begin{pmatrix} \sigma_i & 0 \\ 0 & \sigma_i \end{pmatrix} \tag{2.19}$$

in terms of the Pauli matrices σ_i, and s_v by $(s_v \otimes \mathbb{I}_4\psi)(\boldsymbol{x}) = \psi(\sigma_v\boldsymbol{x})$, the unitary operator associated with the vertical reflection σ_v is determined by

$$S_v = s_v \otimes \Sigma_3. \tag{2.20}$$

To specify the operator implementing rotations around the internuclear axis, let Λ be the projection of the angular momentum operator $\boldsymbol{L} = \boldsymbol{x} \wedge \boldsymbol{p}$ onto the internuclear axis (viz., $\Lambda = L_3$ when we assume the molecule oriented along the z-axis), and Σ_3 the corresponding projection of the spin operator. Combining both projections, $\Omega = \Lambda \otimes \mathbb{I}_4 + \frac{1}{2}\mathbb{I}_{\mathcal{H}} \otimes \Sigma_3$, yields the hermitian generator Ω for the unitary rotation operators $\exp(i\Omega\phi)$. The generator Ω furnishes the generalization of J_3 to nonradially symmetric systems. Obviously, for molecules with total angular momentum $\boldsymbol{J} = \boldsymbol{L} \otimes \mathbb{I}_2 + \mathbb{I}_{\mathcal{H}} \otimes \boldsymbol{\Sigma}$ the operator J^2 no longer commutes with $h(R,\zeta)$ if $R > 0$.

Since they embody symmetry operations, the operators $P_O, S_v, \exp(i\Omega\phi))$ commute with $h(R,\zeta)$. For every eigenvalue $e(R,\zeta)$ of $h(R,\zeta)$, the associated eigenvectors span a subspace invariant under these operators, thus leading to representation spaces for (irreducible) representations of the symmetry group $\boldsymbol{D}_{\infty h}$. These representations can also be employed to mark the eigenvalues, i.e., the PECs $E(R,\zeta) = e(R,\zeta) + \alpha_S^{-1}\zeta^2R^{-1}$ and electronic curves $e(R,\zeta)$. An appropriate label set would include a principal quantum number (to distinguish multiple occurrence of the same irreducible representation), and the eigenvalues of P_O, S_v and Ω. Alternatively, for one-electron systems, together with the (modulus of the) eigenvalues μ of Ω and with parity, one may specify the hydrogenic states that emerge in the UAL [36]. If $\{nlj\}$ denotes such a set of (relativistic) hydrogen quantum numbers (e.g., $1\mathrm{s}_{1/2}$, $2\mathrm{p}_{1/2}$, $2\mathrm{p}_{3/2}$, $\ldots$), then the molecular electronic states are labeled by $\{nlj\}|\mu|_{g,u}$ where the subscripts g(erade) and u(ngerade) indicate the eigenvalues $+1$ and -1 of P_O, respectively, and where one usually adopts the traditional spectroscopic notation $\sigma, \pi, \delta, \ldots$ for $|\mu| = 1/2, 3/2, 5/2, \ldots$.

An important result for the electronic curves follows from the behaviour of $h(R,\zeta)$ under changes of the length scale of its dynamical variable. Let U_a denote the unitary (dilatation) operator on $\mathcal{H}$ that effects the scaling of the $\boldsymbol{x}$-coordinates by $a \in \mathbb{R}$, i.e., $(U_a\psi)(\boldsymbol{x}) = a^{-3/2}\psi(a\boldsymbol{x})$. Then, for $R > 0$

$$U_R h(R,\zeta) U_R^{-1} = R^{-1}\boldsymbol{\alpha}\cdot\boldsymbol{p} + \beta + R^{-1}V_{\mathrm{ne}}(1,\zeta) = R^{-1}\big(h(1,\zeta) + (R-1)\beta\big). \tag{2.21}$$

Since $\|\beta\| = 1$ and thus β is a bounded operator, for all $\psi \in \mathcal{D}(h)$ and $\phi \in \mathcal{H}$,

$$R^{-1}\langle\phi,\, \big(h(1,\zeta) + (R-1)\beta\big)\psi\rangle = R^{-1}\langle\phi,\, h(1,\zeta)\psi\rangle + R^{-1}(R-1)\langle\phi, \beta\psi\rangle \tag{2.22}$$

is obviously an analytic function in R as long as $R \neq 0$. This together with Eq. (2.21) and the independence of the domain of $h(R,\zeta)$ on R implies that $h(R,\zeta)$ is a holomorphic family of type (A) in the sense of Kato [37]. We formulate the consequences as a proposition:

PROPOSITION 2.1. *If for some $R_0 > 0$ the eigenvalue $e(R_0,\zeta) \in (-1,1)$ is nondegenerate (possibly, after restricting to an appropriate symmetry (sub)sector of $\mathcal{D}_{\infty h}$), then there exists a neighbourhood of R_0, such that, for all R in this neighbourhood, $e(R,\zeta)$ is analytic in R with $|e(R,\zeta)| < 1$ and a nondegenerate eigenvalue of $h(R,\zeta)$.*

Analogous results could be derived for the dependence of the energies $e(R,\zeta)$ on the charge parameter ζ; these, however, will not be needed in our investigations here.

2.3. The spectrum in the SAL

As already indicated, physical and numerical experience motivates the expectation that for $R \to \infty$ the molecular energies converge to those of the constituent atoms. For the considered homonuclear one-electron system, the situation becomes particularly simple, because there is only one possible limit, viz., the hydrogen atomic ion with charge ζ separated from a bare proton by an infinite distance. Rigorous results by Harrell and Klaus [38] (formulated for more general potentials) can be transcribed to this special case in the following way:

THEOREM 2.3. *For each atomic energy $\mathrm{e}^{\mathrm{at}}(\zeta) \in \sigma_{\mathrm{pp}}(h^{\mathrm{at}}(\zeta))$ there exist molecular energies $e_j(R,\zeta)$ that have $\mathrm{e}^{\mathrm{at}}(\zeta)$ as their limit, i.e., $\lim_{R\to\infty} e_j(R,\zeta) = \mathrm{e}^{\mathrm{at}}(\zeta)$, where the number of PECs or electronic curves $e_j(R,\zeta)$ converging to $\mathrm{e}^{\mathrm{at}}(\zeta)$ equals the multiplicity of $\mathrm{e}^{\mathrm{at}}(\zeta)$. Conversely, the only accumulation points of $\bigcup_{R>R_l}\sigma_{\mathrm{pp}}(h(R,\zeta))$ for $R_l \to \infty$ are the points of $\sigma_{\mathrm{pp}}(h^{\mathrm{at}}(\zeta)) \cup \{1\}$.*

Besides the proof given in Ref. [38], it also would be possible to derive this theorem by the more "geometrical" techniques employed in the discussion of the SAL within Schrödinger theory [39, 40, 41].

2.4. The UAL lower bound

For molecular Schrödinger operators, also for those with more than one electron and with more than two nuclei, the electronic energies of all states and all nuclear geometries of the molecule can be shown to be bounded below by the electronic ground state energy of the system in the UAL (see, e.g., [42]). The proof of this fact is rather easily achieved by invoking variational arguments, i.e., the minimax principle [43]. Since $h(R, \zeta)$ is not bounded below, here, unfortunately, the standard (Rayleigh-Ritz) variational principles cannot be applied. On the other hand, rigorous variational characterizations for eigenvalues of Dirac (-Coulomb) operators were recently established in the literature [23, 24, 25]. Below, we shall fall back onto the corresponding results of Dolbeau, Esteban, and Séré [23]. Nevertheless, even with these advanced variational tools at disposal, due to the presence of the negative energy (scattering) states, the argumentation cannot simply be adapted from Schrödinger to Dirac Hamiltonians; in case of $h(R, \zeta)$, the demonstration of the UAL lower bound turns out to be distinctly harder than for similar Schrödinger operators.

In the sequel, we encounter the atomic system with the nuclear centre not only located at the origin; thus, with $(\tau_a \psi)(\boldsymbol{x}) := \psi(\boldsymbol{x} - a\boldsymbol{R}_s/|\boldsymbol{R}_s|)$ the unitary translation operator by $a \in \mathbb{R}$ along the unit vector $\boldsymbol{R}_s/|\boldsymbol{R}_s|$), let $h^{\mathrm{at}}(R, \zeta) = \tau_R h^{\mathrm{at}}(\zeta) \tau_R^{-1}$ stand for the atomic Hamiltonian with Coulomb potential centred at $R\,\boldsymbol{R}_s/|\boldsymbol{R}_s|$. Similarly, let $\psi^{\mathrm{at}}(R, \zeta)$ be the corresponding translated atomic ground state eigenfunction(s) obeying $h^{\mathrm{at}}(R, \zeta)\psi^{\mathrm{at}}(R, \zeta) = e^{\mathrm{at}}(\zeta)\psi^{\mathrm{at}}(R, \zeta)$ with $e^{\mathrm{at}}(\zeta) = \sqrt{1 - \zeta^2}$.

To construct the variational representation of the relevant Dirac-Coulomb eigenfunctions by the method of Dolbeau, Esteban, and Séré (DES), it would suggest itself to follow these authors in their choice of the decomposition of $\mathcal{H}$. Namely, defining projections $\theta_\pm$ in terms of the spectral functions

$$\theta_+ = \chi_{(0,\infty)}(T_D), \qquad \theta_- = \chi_{(-\infty,0)}(T_D) \tag{2.23}$$

for the free Dirac operator, the associated subspaces $\mathcal{H}_\pm = \theta_\pm \mathcal{H}$ yield the orthogonal decomposition

$$\mathcal{H} = \mathcal{H}_+ \oplus \mathcal{H}_- \tag{2.24}$$

For these projections and subspaces $\mathcal{H}_\pm$ it is not difficult to obtain a variational characterization of the atomic energies [23]; completely analogous arguments also produce variational formulas for the energies of the molecular

Hamiltonian. Unfortunately, however, we could not figure out any reasonably feasible way to relate the resulting variational atomic and molecular expressions such that a UAL lower bound can be deduced.

Therefore, here we resort to an alternative decomposition of $\mathcal{H}$ into positive and negative subspaces $\mathcal{H}_\pm^{\rm at} = \theta_\pm^{\rm at}\mathcal{H}$ by defining projections $\theta_\pm^{\rm at}$ with the help of the atomic spectral functions

$$\theta_+^{\rm at} = \chi_{(0,\infty)}\big(h^{\rm at}(R/2, 2\zeta)\big), \qquad \theta_-^{\rm at} = \chi_{(-\infty,0)}\big(h^{\rm at}(R/2,\, 2\zeta)\big). \qquad (2.25)$$

Furthermore, let $\mathcal{F}$ be a core for $h^{\rm at}(R/2,\, 2\zeta)$; since below we have to restrict the ζ-range to $(0, \zeta_{\rm max})$ with $\zeta_{\rm max} < \sqrt{3}/4$, we may take $\mathcal{F} = \mathcal{D}(|T_D|^{1/2})$ without any problems. As for $\mathcal{H}$, also $\mathcal{F} = \mathcal{F}_+ \oplus \mathcal{F}_-$ is decomposed into the orthogonal sum of subspaces $\mathcal{F}_\pm = \theta_\pm^{\rm at}\mathcal{F} \subset \mathcal{H}_\pm$. To keep the notation succinct, we will write $[A]_\psi := \langle\psi,\, A\psi\rangle/\langle\psi,\psi\rangle$ for the normalized expectation value of an operator A within the state $\psi \in \mathcal{D}(A)$, $\psi \neq 0$.

In case of the atomic Hamiltonian, our particular choice of projections (2.25) renders the verification of the prerequisites for the DES variational representation almost trivial. Clearly, by construction,

$$\sup_{\phi_- \in \mathcal{F}_- \setminus\{0\}} [h^{\rm at}(R/2,\, 2\zeta)]_{\phi_-} \leq 0 \qquad (2.26)$$

and thus assumption (ii) of theorem 1.1 of DES [23] (reproduced as theorem A.1 in the appendix for easy reference) is satisfied. The validity of assumption (iii) for that theorem is a consequence of

$$\begin{aligned} \lambda^{\rm at}(2\zeta) &:= \inf_{\phi_+ \in \mathcal{F}_+} \sup_{\substack{\psi = \phi_+ \oplus \phi_- \neq 0 \\ \phi_- \in \mathcal{F}_-}} [h^{\rm at}(R/2,\, 2\zeta)]_\psi \\ &\geq \inf_{\phi_+ \in \mathcal{F}_+ \setminus\{0\}} [h^{\rm at}(R/2,\, 2\zeta)]_{\phi_+} \;=\; e^{\rm at}(2\zeta) \;>\; 0 \end{aligned} \qquad (2.27)$$

where the second line follows from the first one by "freezing" $\phi_- = 0$ to bound the sup from below. Theorem 1.1 of DES then assures that the expression (2.27) for $\lambda^{\rm at}(2\zeta)$ indeed furnishes the correct variational representation of the UAL atomic ground state energy (i.e., in (2.27) the inequality can be replaced by an equality). The corresponding characterization of the molecular energies for $R > 0$ requires additional arguments and is formulated in the next lemma.

LEMMA 2.1. *Define $\zeta_{\rm max}$ as the real root of the polynomial $4x^3 - x^2 + x - 1/8$; consider*

$$\begin{aligned} &\zeta \in (0, \zeta_{\rm max}), \\ &\zeta_{\rm max} = \tfrac{1}{12}\Big(1 + \sqrt[3]{10 + 3\sqrt{159}} - \sqrt[3]{-10 + 3\sqrt{159}}\Big) \approx 0.1333 \end{aligned} \qquad (2.28)$$

and $\mathcal{F}_\pm$ constructed from the atomic projections $\theta_\pm^{\rm at}$ in (2.25). Then the ground state energy of $h(R,\zeta)$ can be expressed as

$$e_0(R,\zeta) = \inf_{\phi_+\in\mathcal{F}_+} \sup_{\substack{\psi=\phi_+\oplus\phi_-\neq 0\\ \phi_-\in\mathcal{F}_-}} [h(R,\,\zeta)]_\psi. \tag{2.29}$$

Proof. The proof of lemma 2.2 consists of verifying the prerequisites that allow the application of a "continuation" theorem (viz., theorem 3.1 from DES [23], summarized in theorem A.2 in the appendix). Since in this theorem perturbations of T_D by a family of bounded operators are studied, we start by treating appropriately regularized versions $V_{\rm ne}^\varepsilon(R,\mu)$, $0\le\mu\le\zeta<\zeta_{\max}$, of the molecular potentials, where the Coulomb singularities $|\boldsymbol{x}\pm\boldsymbol{R}/2|^{-1}$ are replaced by bounded functions $\big(|\boldsymbol{x}\pm\boldsymbol{R}/2|+\varepsilon\big)^{-1}$; eventually, the limit $\varepsilon\downarrow 0$ will be taken.

Our first goal is to show

$$\sup_{\phi_-\in\mathcal{F}_-\setminus\{0\}} [T_D]_{\phi_-} \le 0 \tag{2.30}$$

for all $0<\zeta<\zeta_{\max}$. Due to the negativity $[V_{\rm ne}^\varepsilon(R,\mu)]_\psi\le 0$, inequality (2.30) then immediately implies

$$\sup_{\phi_-\in\mathcal{F}_-\setminus\{0\}} [h(R,\mu)]_{\phi_-} \le 0 \tag{2.31}$$

for all $0\le\mu\le\zeta$. To prove (2.30), we invoke a relation between the kinetic part of the Dirac operators and the atomic projections put forward by Griesemer, Lewis, and Siedentop; in Ref. [25] (Corollary 1) these authors established the bound

$$||\;|T_D|^{1/2}\theta_+\theta_-^{\rm at}|T_D|^{-1/2}\;|| \le c_\zeta \tag{2.32}$$

for $0<\zeta<1/4$, and where $c_\zeta = 2\zeta(1-4\zeta)^{-1}\sqrt{1+4\zeta}$. For all $\psi\in\mathcal{D}\big(|T_D|^{1/2}\big)\cap{\rm Ran}(\theta_-^{\rm at})$ the bound (2.32) entails

$$\langle\theta_-^{\rm at}\psi,\,\theta_+|T_D|\theta_+\theta_-^{\rm at}\psi\rangle \le c_\zeta^2\langle\psi,\,\theta_-^{\rm at}|T_D|\theta_-^{\rm at}\psi\rangle. \tag{2.33}$$

Thus we can estimate

$$\begin{aligned}\theta_-^{\rm at}|T_D|\theta_-^{\rm at} &= \theta_-^{\rm at}\theta_+|T_D|\theta_+\theta_-^{\rm at} \;+\; \theta_-^{\rm at}\theta_-|T_D|\theta_-\theta_-^{\rm at}\\ &\le (1-c_\zeta^2)^{-1}\theta_-^{\rm at}\theta_-|T_D|\theta_-\theta_-^{\rm at}\end{aligned} \tag{2.34}$$

and

$$\theta_-^{\rm at}\theta_+|T_D|\theta_+\theta_-^{\rm at} \le c_\zeta^2(1-c_\zeta^2)^{-1}\theta_-^{\rm at}\theta_-|T_D|\theta_-\theta_-^{\rm at}. \tag{2.35}$$

For T_D this means

$$\begin{aligned}\theta_-^{\mathrm{at}} T_D \theta_-^{\mathrm{at}} &= \theta_-^{\mathrm{at}} \theta_+ T_D \theta_+ \theta_-^{\mathrm{at}} \; + \; \theta_-^{\mathrm{at}} \theta_- T_D \theta_- \theta_-^{\mathrm{at}} \\ &\leq (1 - c_\zeta^2)^{-1} (1 - 2c_\zeta^2) \theta_-^{\mathrm{at}} \theta_- T_D \theta_- \theta_-^{\mathrm{at}} \leq 0\end{aligned} \tag{2.36}$$

as long as $1 - 2c_\zeta^2 > 0$, i.e., as long as ζ obeys the condition specified in (2.28). Hence estimates (2.30) and (2.31) hold, and we can set $a_- = 0$ in theorem A.2.

To verify the next assumption for theorem A.2, viz., the existence of a constant $a_+ > a_-$ such that all eigenvalues $e_k^\varepsilon(R,\mu)$ of $h^\varepsilon(R,\mu) = T_D + V_{\mathrm{ne}}^\varepsilon(R,\mu)$ remain above this constant, $e_k^\varepsilon(R,\mu) \geq a_+$, we observe that the $e_k^\varepsilon(R,\mu)$ are bounded below by the eigenvalues of the corresponding Brown-Ravenhall operators (theorem A.3 in the appendix). In fact, due to the monotonicity of the potentials in ε, we may take the Brown-Ravenhall operators with $\varepsilon = 0$. Moreover, since for the Brown-Ravenhall Hamiltonian it is easy (like for Schrödinger operators) to demonstrate a UAL lower bound, we infer

$$e_k^\varepsilon(R,\mu) \geq e_{\mathrm{BR}}(R,\mu) \geq e_{\mathrm{BR}}^{\mathrm{at}}(2\mu) \geq e_{\mathrm{BR}}^{\mathrm{at}}(2\zeta_{\max}) =: a_+. \tag{2.37}$$

for all $\varepsilon \geq 0$, $R \geq 0$, $0 \leq \mu \leq \zeta \leq \zeta_{\max}$. Then, $a_+ > 0$, because the atomic Brown-Ravenhall ground state energy $e_{\mathrm{BR}}^{\mathrm{at}}(2\zeta_{\max})$ is known to be strictly positive [66] if $2\zeta_{\max} \leq 2/(\frac{\pi}{2} + \frac{2}{\pi})$.

For the last assumption in theorem A.2 we have to show

$$\inf_{\phi_+ \in \mathcal{F}_+} \sup_{\substack{\psi = \phi_+ \oplus \phi_- \neq 0 \\ \phi_- \in \mathcal{F}_-}} [T_D]_\psi \; > \; a_-. \tag{2.38}$$

However, since adding the (atomic) potential gives a negative contribution, inequality (2.38) follows directly from

$$\begin{aligned}\inf_{\phi_+ \in \mathcal{F}_+} \sup_{\substack{\psi = \phi_+ \oplus \phi_- \neq 0 \\ \phi_- \in \mathcal{F}_-}} [T_D]_\psi \; &\geq \; \inf_{\phi_+ \in \mathcal{F}_+ \setminus \{0\}} [T_D]_{\phi_+} \\ &\geq \; \inf_{\phi_+ \in \mathcal{F}_+ \setminus \{0\}} [h^{\mathrm{at}}(R/2,\, 2\zeta)]_{\phi_+} \; = \; e^{\mathrm{at}}(2\zeta) \; > \; 0\end{aligned} \tag{2.39}$$

as in (2.27).

Now, with all prerequisites for theorem A.2 being met, we can continue from $\mu = 0$ to $\mu = \zeta < \zeta_{\max}$, and, by employing the same limiting arguments as in [23] when $\varepsilon \downarrow 0$, we can deduce the correctness of the expression (2.29) for the molecular ground state energy. ▮

With the variational representation (2.29) at our disposal, the derivation of the lower bound property of the UAL energies becomes fairly straightforward. Recalling that all eigenstates of $h(R,\zeta)$ can be chosen to enjoy a definite parity, in (2.29) we can restrict variations to subspaces of even or odd parity. Thus, using $P_O h^{\rm at}(-R/2,\, 2\zeta) P_O = h^{\rm at}(R/2,\, 2\zeta)$, in the first case (and similarly for odd parity)

$$
\begin{aligned}
e_0(R,\zeta) &= \inf_{\phi_+\in\mathcal{F}_+} \sup_{\substack{\psi=\phi_+\oplus\phi_-\neq 0\\ P_O\psi=\psi,\ \phi_-\in\mathcal{F}_-}} [h(R,\,\zeta)]_\psi \\
&= \inf_{\phi_+\in\mathcal{F}_+} \sup_{\substack{\psi=\phi_+\oplus\phi_-\neq 0\\ P_O\psi=\psi,\ \phi_-\in\mathcal{F}_-}} \Big(\tfrac{1}{2}[h^{\rm at}(-R/2,\,2\zeta)]_\psi + \tfrac{1}{2}[h^{\rm at}(R/2,\,2\zeta)]_\psi\Big) \\
&= \inf_{\phi_+\in\mathcal{F}_+} \sup_{\substack{\psi=\phi_+\oplus\phi_-\neq 0\\ P_O\psi=\psi,\ \phi_-\in\mathcal{F}_-}} [h^{\rm at}(R/2,\,2\zeta)]_\psi \\
&\geq \inf_{\substack{\phi_+\in\mathcal{F}_+\setminus\{0\}\\ P_O\phi_+=\phi_+}} [h^{\rm at}(R/2,\,2\zeta)]_{\phi_+} \\
&\geq \inf_{\phi_+\in\mathcal{F}_+\setminus\{0\}} [h^{\rm at}(R/2,\,2\zeta)]_{\phi_+} \;=\; e^{\rm at}(2\zeta)
\end{aligned}
\tag{2.40}
$$

where the last inequality results from enlarging the set of ϕ_+. By estimate (2.40) we have proved:

THEOREM 2.4. *If $0<\zeta<\zeta_{\rm max}$ as specified in (2.28) and $R\geq 0$, then the molecular ground state energy cannot be lower than the ground state energy of the UAL,*

$$
e_0(R,\,\zeta) \geq e^{\rm at}(2\zeta). \tag{2.41}
$$

While our methods are not strong enough to demonstrate (2.41) for $\zeta\geq\zeta_{\rm max}$, we conjecture that the UAL lower bound continues to hold for all $\zeta\in(0,1/2)$, independently of whether the variational expression (2.29) and lemma 2.2 can be extended beyond $\zeta_{\rm max}$.

3. REGULARITY OF THE ELECTRONIC CURVES

3.1. Continuity

The scaling procedure leading to the analyticity properties formulated in proposition 2.1 are not applicable if $R=0$. In view of the drastic change of the self-adjointness behaviour of $h(R,\zeta)$ (cf. theorems 2.1 and 2.2) in the UAL, a priori even the continuity of the electronic curves may appear unpredictable for $R\downarrow 0$. To recover this continuity at least for $\zeta\in(0,1/2)$ will be our next goal; here, if $\sqrt{3}/2<2\zeta<1$, we shall adopt the self-adjoint extension described in part (ii) of theorem 2.1 for $h^{\rm at}(2\zeta)$.

THEOREM 3.1. *If $0 < \zeta < 1/2$, the molecular operator $h(R,\zeta)$ converges to the UAL operator $h^{\mathrm{at}}(2\zeta)$ in norm resolvent sense, $h(R,\zeta) \xrightarrow{\mathrm{n.r.}} h^{\mathrm{at}}(2\zeta)$ as $R \downarrow 0$.*

Proof. The above assertion extends results by Klaus [19] in which the norm resolvent convergence was shown if $0 < \zeta < 1/\pi$; for the remaining interval $1/\pi \le \zeta < 1/2$, a technical problem forced Klaus to exclude a countable set $\{\zeta_i\}$ of "critical" coupling parameters ζ_i so that the norm resolvent convergence could only be demonstrated if $\zeta \neq \zeta_i$. However, it was conjectured that actually this set $\{\zeta_i\}$ is empty [19]. Here, our proof follows the general strategy of Klaus' reasoning; at a certain point, though, some alternative arguments allow simplifications and an extension of the ζ-range. While we refer for details to the original article [19], a comprehensible presentation requires the repetition of the essential steps of Klaus' argumentation.

Let

$$K_\zeta(R,E) = \zeta\sqrt{-V_{\mathrm{ne}}(R,1)}(T_D - E)^{-1}\sqrt{-V_{\mathrm{ne}}(R,1)} \tag{3.1}$$

stand for the Birman-Schwinger operator associated with $h(R,\zeta)$. With the help of K, for all E such that the spectrum of $K_\zeta(R,E)$ does not contain -1, the resolvent of $h(R,\zeta)$ can be expressed as

$$\begin{aligned}\big(h(R,\zeta) - E\big)^{-1} = (T_D - E)^{-1} + (T_D - E)^{-1}\sqrt{-V_{\mathrm{ne}}(R,1)}\times \\ \big(1 - K_\zeta(R,E)\big)^{-1}\sqrt{-V_{\mathrm{ne}}(R,1)}(T_D - E)^{-1}\end{aligned} \tag{3.2}$$

Clearly, $E = 0$ belongs to the resolvent set of T_D, $0 \in \rho(T_D)$. Since $V_{\mathrm{ne}}(R,1)$ converges strongly to $V_{\mathrm{ne}}(0,1)$ as $R \downarrow 0$, also

$$K_\zeta(R,0) \to K_\zeta(0,0) \tag{3.3}$$

in the strong sense. Furthermore, lemma 5.2 of Ref. [19] states that

$$\begin{aligned}\sqrt{-V_{\mathrm{ne}}(R,1)}T_D^{-1} &\to \sqrt{-V_{\mathrm{ne}}(0,1)}T_D^{-1} \\ T_D^{-1}\sqrt{-V_{\mathrm{ne}}(R,1)} &\to T_D^{-1}\sqrt{-V_{\mathrm{ne}}(0,1)}\end{aligned} \tag{3.4}$$

in norm as $R \downarrow 0$. As long as the resolvent $\big(1 - K_\zeta(R,0)\big)^{-1}$ is defined for all $R \ge 0$ in a neighbourhood $\mathcal{U}_0 \neq \emptyset$ of zero, i.e., as long as $1 \in \rho\big(K_\zeta(R,0)\big)$, relation (3.3) implies the strong convergence

$$\big(1 - K_\zeta(R,0)\big)^{-1} \to \big(1 - K_\zeta(0,0)\big)^{-1} \tag{3.5}$$

for $R \downarrow 0$. Hence, using that $\sqrt{-V_{\rm ne}(R,1)}T_D^{-1}$ and thus also $\big(1-K_\zeta(R,0)\big)^{-1}\times \sqrt{-V_{\rm ne}(R,1)}T_D^{-1}$ are compact operators, and, by (3.4), converge in norm, from the second relation in (3.4) we conclude that when $R \downarrow 0$ the product

$$\begin{aligned} &T_D^{-1}\sqrt{-V_{\rm ne}(R,1)}\big(1-K_\zeta(R,0)\big)^{-1}\sqrt{-V_{\rm ne}(R,1)}T_D^{-1} \\ &\quad\to\ T_D^{-1}\sqrt{-V_{\rm ne}(0,1)}\big(1-K_\zeta(0,0)\big)^{-1}\sqrt{-V_{\rm ne}(0,1)}T_D^{-1} \end{aligned} \tag{3.6}$$

also converges in norm. Therefore, the norm convergence of (3.1) and the assertion of theorem 3.1 can be deduced from (3.6) as soon as we have confirmed that for all $R \geq 0$, $R \in \mathcal{U}_0$,

$$1 \in \rho\big(K_\zeta(R,0)\big). \tag{3.7}$$

As observed by Klaus, if $0 < \zeta < 1/\pi$ the relation (3.7) follows from the inequality (lemma 5.1 in Ref. [19])

$$\|\sqrt{-V_{\rm ne}(R,1)}T_D^{-1}\sqrt{-V_{\rm ne}(R,1)}\| \leq \pi. \tag{3.8}$$

Here, we infer (3.7) for all $0 < \zeta < 1/2$ from the subsequent lemma. ▮

Lemma 3.1. *Let $P_\Omega(K)$ denote the projection-valued measure associated with the self-adjoint operator K. If $0 < \zeta < 1/2$ and $-1 < E \leq 0$, then there exists a nonvoid neighbourhood $\mathcal{U}_0 \neq \emptyset$ of $R = 0$ such that for all $R \in \mathcal{U}_0$ with $0 \leq R < \infty$*

$$\dim P_{(\zeta,\infty)}\big(K_\zeta(R,E)\big) = 0. \tag{3.9}$$

Proof. This result is the analogue of proposition E-(iii) in section 2 of Ref. [19]; so, again, we can mostly mimic the reasoning by Klaus. First, since for $-1 < E \leq 0$ the bound $K_\zeta(R,E) \leq K_\zeta(R,0)$ holds, it is sufficient to restrict attention to $K_\zeta(R,0)$. Assuming

$$\dim P_{(\zeta,\infty)}\big(K_\zeta(R,0)\big) > 0, \tag{3.10}$$

for some $0 < \zeta < 1/2$ and some $R \geq 0$, we want to derive a contradiction. Inequality (3.10) implies the existence of an eigenvalue $\lambda \in (\zeta,\infty)$ of $K_\zeta(R,0)$, and, after scaling, the existence of the eigenvalue 1 for the operator $K_\mu(R,0)$ with $\mu = \zeta/\lambda \leq \zeta$. By the Birman-Schwinger principle [44, 45], this is equivalent to

$$0 \in \sigma_{\rm d}\big(h(R,\mu)\big), \tag{3.11}$$

i.e., to the existence of an eigenvalue $e(R,\mu)=0$ for the electronic Hamiltonian $h(R,\mu)$. Let ψ_0 be the associated zero-energy eigenstate, chosen to have a definite parity. Furthermore, we denote by $V_{\rm ne}^{\pm}(R,\mu)$ the multiplication operators $\big(V_{\rm ne}^{-}(R,\mu)\psi\big)(\boldsymbol{x}) = -\mu|\boldsymbol{x} \pm \frac{1}{2}\boldsymbol{R}_s|^{-1}\psi(\boldsymbol{x})$ such that $V_{\rm ne} = V_{\rm ne}^{+} + V_{\rm ne}^{-}$. For any given $\varepsilon > 0$, the following weight function

$$w(\boldsymbol{x}) = \begin{cases} \varepsilon|\boldsymbol{x}| & \text{if} \quad |\boldsymbol{x}| \le \varepsilon^{-1} \\ 1 & \text{if} \quad |\boldsymbol{x}| \ge \varepsilon^{-1} \end{cases} \tag{3.12}$$

was introduced by Wüst and led to a relation between the weighted kinetic and Coulomb parts of the atomic Dirac Hamiltonian (lemma 3 in Ref. [32]). To apply a specialized version of Wüst's inequality (Eq. (20) in [32]) to the molecular situation, viz.,

$$||\, w^{1/2} T_D \psi \,||^2 \;\ge\; (1-\varepsilon^2/4)\, ||\, w^{1/2}|\boldsymbol{x}|^{-1}\psi \,||^2 \tag{3.13}$$

if $0<\varepsilon<2$ and $\psi \in H^1(\mathbb{R}^3,\mathbb{C}^4)$, we translate w along the internuclear axis. With $w_{\pm} := \tau_{\pm R/2} w(\tau_{\pm R/2})^{-1}$ regarded as multiplication operators, inequality (3.13) can be recast into

$$||\, w_+^{1/2} T_D \psi \,|| \;\ge\; \sqrt{1-\varepsilon^2/4}\, \mu^{-1} ||\, w_+^{1/2} V_{\rm ne}^{+}(R,\mu)\psi \,||. \tag{3.14}$$

Employing (3.14), we estimate for $0<R<\infty$

$$\begin{aligned} 0 \;=\; & ||w_+^{1/2} h(R,\mu)\psi_0|| \\ & \ge ||w_+^{1/2} T_D\psi_0|| - ||w_+^{1/2} V_{\rm ne}^{+}(R,\mu)\psi_0|| - ||w_+^{1/2} V_{\rm ne}^{-}(R,\mu)\psi_0|| \\ & \ge 2\big(\sqrt{1-\varepsilon^2/4}/(2\mu) - 1\big)\, ||w_+^{1/2} V_{\rm ne}^{+}(R,\mu)\psi_0|| \,+ \\ & \qquad\qquad ||w_+^{1/2} V_{\rm ne}^{+}(R,\mu)\psi_0|| - ||w_+^{1/2} V_{\rm ne}^{-}(R,\mu)\psi_0|| \end{aligned} \tag{3.15}$$

where in the first line at the RHS all terms are well defined since $0<\mu<1/2$ (and therefore $\psi_0 \in \mathcal{D}(V_{\rm ne}^{\pm})$). Now, ψ_0 being an eigenstate of the parity operator P_O, the equality $||w_+^{1/2} V_{\rm ne}^{+}(R,\mu)\psi_0|| = ||w_-^{1/2} V_{\rm ne}^{+}(R,\mu)\psi_0||$ and the bound

$$\begin{aligned} \big|\, ||w_+^{1/2} V_{\rm ne}^{+}(R,\mu)\psi_0|| - ||w_-^{1/2} V_{\rm ne}^{+}(R,\mu)\psi_0|| \,\big| \;\le\; & ||w_+ - w_-||_\infty \times \\ & \frac{||V_{\rm ne}^{+}(R,\mu)\psi_0||^2}{||w_+^{1/2} V_{\rm ne}^{+}(R,\mu)\psi_0|| + ||w_-^{1/2} V_{\rm ne}^{+}(R,\mu)\psi_0||} \end{aligned} \tag{3.16}$$

together with $||w_+ - w_-||_\infty = \varepsilon R$ ensue a contradiction in Eq. (3.15) if ε is chosen such that $\sqrt{1-\varepsilon^2/4} > 2\mu$ and R is confined to the interval $(0,R_\varepsilon)$ with R_ε sufficiently small. If $R=0$, the energies are explicit, $e(0,\mu) =$

$\sqrt{1-(2\mu)^2}$. Hence, if μ obeys $0<\mu<1/2$, there is a neighbourhood $\mathcal{U}_0$ of $R=0$ (that in our construction also depends on μ) such that the molecular Hamiltonians $h(R,\mu)$ only have nonvanishing eigenvalues, which contradicts (3.11) for these R. ▌

It may be worth to point out that the arguments above for the absence of zero-energy eigenstates can also be utilized to show the nonexistence of negative eigenvalues for one-centre potentials and would considerably facilitate and shorten the relevant analysis in Ref. [34] (for details, cf. the appendix). Strictly positive lower bounds on $e(R,\zeta)$ provide alternative – though rather direct – procedures to rule out molecular zero-energy bound states in lemma 3.1. If we invoke the UAL lower bound (2.41), this, unfortunately, would only cover charge parameters up to the $\zeta_{\max}$ given in (2.28). Larger ζ up to $\zeta\le(\frac{\pi}{2}+\frac{2}{\pi})^{-1}\approx 0.4530$ can be reached if the UAL ground state energy of the (atomic) Brown-Ravenhall Hamiltonian is taken as lower bound (see theorem A.3 and the discussion in the appendix). Compared with the maximal $\zeta=1/\pi\approx 0.3183$ allowed by Klaus' original method, this is already quite an improvement. Of course, the conjectured extension of the UAL lower bound to all $0<\zeta<1/2$ would immediately disprove the existence of molecular zero-energy eigenstates for these ζ; here, from the continuity of the electronic curves and the positivity of the UAL energies we only can infer the existence of a $R_p>0$ such that $e(R,\zeta)>0$ for all $\zeta\in(0,1/2)$ and $0\le R<R_p$.

3.2. Differentiability

The norm resolvent convergence of $h(R,\zeta)$ established in theorem 3.1 entails continuity of the eigenvalues $e(r,\zeta)$ and their total projections as $R\downarrow 0$ (see theorem VIII.23 in Ref. [46]). Thus we know that the electronic curves $e(R,\zeta)$ are continuous functions of $R\ge 0$, and analytic away from $R=0$. Our next aim is to demonstrate that $e(R,\zeta)$ are actually once differentiable also at $R=0$.

THEOREM 3.2. *Let $0<\zeta<1/2$. Then for all $R\ge 0$ and $E\in\rho\big(h(R,\zeta)\big)$ the resolvent $\big(h(R,\zeta)-E\big)^{-1}$ is strongly continuously differentiable in R.*

Proof. To deduce the assertion, we have to verify the strong convergence of

$$(\Delta R)^{-1}\big((h(R+\Delta R,\,\zeta)-E)^{-1}-(h(R,\,\zeta)-E)^{-1}\big)\;=\;(\Delta R)^{-1}\times \big(h(R+\Delta R,\,\zeta)-E\big)^{-1}\big(h(R+\Delta R,\,\zeta)-h(R,\,\zeta)\big)\big(h(R,\,\zeta)-E\big)^{-1} \tag{3.17}$$

for $\Delta R \to 0$, or, if $R = 0$, for $\Delta R \downarrow 0$. With the help of the unitary translation operator $\tau_{\Delta R}$ we can rewrite the difference on the RHS of equation (3.17) as

$$\begin{aligned} h(R+\Delta R,\,\zeta) - h(R,\,\zeta) &= V_{\rm ne}(R+\Delta R,\,\zeta) - V_{\rm ne}(R,\,\zeta) \\ &= \tau_{\Delta R} V^+_{\rm ne}(R,\zeta)\tau^{-1}_{\Delta \rm R} - V^+_{\rm ne}(R,\zeta) + \tau_{\Delta R} V^-_{\rm ne}(R,\zeta)\tau^{-1}_{\Delta \rm R} - V^-_{\rm ne}(R,\zeta) \\ &= \tau_{\Delta R} V^+_{\rm ne}(R,\zeta)(\tau^{-1}_{\Delta R} - 1) + (\tau_{\Delta R} - 1)V^+_{\rm ne}(R,\zeta) \\ &\qquad + \tau^{-1}_{\Delta R} V^-_{\rm ne}(R,\zeta)(\tau_{\Delta R} - 1) + (\tau^{-1}_{\Delta R} - 1)V^-_{\rm ne}(R,\zeta) \end{aligned} \tag{3.18}$$

where $V^{\pm}_{\rm ne}(R,\zeta)$ are the multiplication operators defined in the preceding section 3.1. On the domain $\mathcal{D}(\boldsymbol{p})$ of the momentum operator we have

$$(\Delta R)^{-1}(\tau_{\Delta R} - 1) = (\Delta R)^{-1}\big(\exp(-i\Delta R\, p_s) - 1\big) = -ip_s + \mathcal{O}(\Delta R), \tag{3.19}$$

with $p_s = |\boldsymbol{R}_s|^{-1}\boldsymbol{R}_s{\cdot}\boldsymbol{p}$ being the projection of the momentum onto the internuclear axis. Thus, $(\Delta R)^{-1}(\tau_{\Delta R} - 1) \to -ip_s$, and, analogously, $(\Delta R)^{-1}(\tau^{-1}_{\Delta R} - 1) \to ip_s$ converge strongly as $\Delta R \to 0$. Focusing first onto the terms containing $V^+_{\rm ne}$, and using that $\tau_{\Delta R}$ and $(T_D - 1)^{-1}$ commute, the expression

$$\begin{aligned} \big(h(R{+}\Delta R,\,\zeta) - E\big)^{-1}&\tau_{\Delta R} V^+_{\rm ne}(R,\zeta)(\Delta R)^{-1}(\tau^{-1}_{\Delta R} - 1)\big(h(R,\,\zeta) - E\big)^{-1} \\ &= \big(h(R+\Delta R,\,\zeta) - E\big)^{-1}(T_D - E)\tau_{\Delta R}(T_D - E)^{-1}V^+_{\rm ne}(R,\zeta)\times \\ &\qquad (\Delta R)^{-1}(\tau^{-1}_{\Delta R} - 1)\big(h(R,\,\zeta) - E\big)^{-1} \end{aligned} \tag{3.20}$$

is recognized to be a product of bounded operators; here, due to the norm resolvent continuity of $h(R,\zeta)$, the first factor converges strongly to $\big(h(R,\zeta) - E\big)^{-1}(T_D - E)$, while as a consequence of (3.19) the last factor has $-ip_s\big(h(R,\zeta) - E\big)^{-1}$ as its strong limit; moreover, $\tau_{\Delta R} \to \mathbb{I}_{\mathcal{H}}$ strongly for $\Delta R \to 0$. In the same way, in

$$\begin{aligned} \big(h(R{+}\Delta R,\,\zeta) - E\big)^{-1}&(\Delta R)^{-1}(\tau_{\Delta R} - 1)V^+_{\rm ne}(R,\zeta)\big(h(R,\,\zeta) - E\big)^{-1} \\ &= \big(h(R+\Delta R,\,\zeta) - E\big)^{-1}(T_D - E)(\Delta R)^{-1}(\tau_{\Delta R} - 1)(T_D - E)^{-1}\times \\ &\qquad V^+_{\rm ne}(R,\zeta)\big(h(R,\,\zeta) - E\big)^{-1} \end{aligned} \tag{3.21}$$

the factor $(\Delta R)^{-1}(\tau_{\Delta R} - 1)(T_D - E)^{-1}$ is a bounded operator that converges strongly to $ip_s(T_D - E)^{-1}$. Completely analogous arguments hold for terms containing $V^-_{\rm ne}$. Therefore, equations (3.20) and (3.21) and their counterparts for $V^-_{\rm ne}$ together with (3.18) prove the strong convergence of the expression (3.17). Furthermore, combining the formulas, the derivative of the resolvent becomes

$$\frac{\partial}{\partial R}\big(h(R,\,\zeta)-E\big)^{-1}=\big(h(R,\zeta)-E\big)^{-1}\big(-i(p_sV_{\rm ne}^{+}(R,\zeta))\\ +i(p_sV_{\rm ne}^{-}(R,\zeta))\big)\big(h(R,\,\zeta)-E\big)^{-1}; \tag{3.22}$$

since $p_sV_{\rm ne}^{+}(0,\zeta)=p_sV_{\rm ne}^{-}(0,\zeta)$, equation (3.22) reveals that at $R=0$ the derivative vanishes. From the RHS of (3.22) we also can deduce the strong continuity when $R\downarrow 0$. Namely, both factors $\big(h(R,\,\zeta)-E\big)^{-1}p_s$ and $V_{\rm ne}^{\pm}(R,\zeta)\big(h(R,\,\zeta)-E\big)^{-1}$ converge strongly as bounded operators in this limit, where, in turn, the convergence of the latter factor is easily seen by writing it as a product of $V_{\rm ne}^{\pm}(R,\zeta)\big(T_D-E\big)^{-1}$ and $\big(T_D-E\big)\big(h(R,\,\zeta)-E\big)^{-1}$. ▮

We summarize the consequences of the preceding results for the regularity of electronic curves and eigenfunctions:

Corollary 3.1. *Assume* $0<\zeta<1/2$.
(i) If for $R_0\geq 0$ *the energy* $e(R_0,\zeta)\in\sigma_{\rm d}\big(h(R,\zeta)\big)$ *is a nondegenerate eigenvalue of* $h(R_0,\zeta)$, *then* $e(R,\zeta)$ *is at least once continuously differentiable in* R *on a neighbourhood of* R_0; *if* $R_0>0$, *then* $e(R,\zeta)$ *is analytic. Moreover, the electronic curves arrive at* $R=0$ *with a horizontal tangent, that is,* $\lim_{R\downarrow 0}\frac{\partial e}{\partial R}(R,\zeta)=0$.
(ii) If $P(R_0,\zeta)$ *stands for the total projection associated with* $e(R_0,\zeta)\in\sigma_{\rm d}\big(h(R,\zeta)\big)$, *then* $P(R,\zeta)$ *is at least once continuously differentiable in* R *on a neighbourhood of* R_0.

Proof. Given the results in chapter 2 and 3, the assertions of the corollary ensue from application of standard theorems (see section VIII.7 in Ref. [46], and VII §3.1 in [37]). Concerning the behaviour around $R=0$ we recall that –after reducing the atomic Hamiltonian by its full symmetry group – the atomic energies are nondegenerate on the irreducible subspaces; whence, for sufficiently small $R>0$, the molecular energies, too, are nondegenerate on their symmetry subspaces. Furthermore, for (ii), we observe that there exists a circle $\Gamma(R_0)$ around R_0 such that for all $R\in\mathcal{N}(R_0)$ from a neighbourhood $\mathcal{N}(R_0)$ of R_0 we have $\Gamma(R_0)\subset\rho\big(h(R,\zeta)\big)$ and $\Gamma(R_0)\cap\overline{\bigcup_{R\in\mathcal{N}(R_0)}\sigma\big(h(R,\zeta)\big)}=\emptyset$. With the circle $\Gamma(R_0)$ the total projection can be expressed as contour integral,

$$P(R,\zeta)=-\tfrac{1}{2\pi i}\int_{\Gamma(R_0)}dE\,\big(h(R,\,\zeta)-E\big)^{-1}, \tag{3.23}$$

so that the differentiability of $P(R,\zeta)$ follows from the differentiability of the resolvent. ▮

For Schrödinger operators with the kinetic energy containing the second derivatives with respect to the electronic coordinates, it is known [40] that the resolvent at $R = 0$ is not solely once, but twice differentiable in R. Indeed, the occurrence of second derivatives in the Schrödinger Hamiltonian provides the crucial tool to control the terms analogous to (3.12) that arise when the resolvent is derived twice with respect to R; a kinetic energy linear in the momentum – like T_D, the Dirac one – is not sufficient for that purpose. Hence, one cannot expect to extend theorem 3.2 and corollary 3.1 to second derivatives in R.

3.3. Feynman-Hellman theorem

A rather immediate consequence of the regularity of the projections for the electronic curves is the Feynman-Hellman theorem that simplifies the derivative of energy expectation values within eigenstates of the Hamiltonian. The formulation below also covers the degenerate case.

THEOREM 3.3. *For $0 < \zeta < 1/2$ and $0 \leq R_0$ let $e(R_0,\zeta) \in \sigma_{\mathrm{d}}\big(h(R_0,\zeta)\big)$ be a discrete eigenvalue of $h(R_0,\zeta)$, and $P(R_0,\zeta)$ the associated total projection. We denote by $e_j(R,\zeta)$, $j = 1,\ldots,d$ the eigenvalues of $P(R,\zeta)h(R,\zeta)$ $P(R,\zeta)$ for R in a neighbourhood of R_0. Then the eigenvalues λ_j of $P(R_0,\zeta)(\partial h/\partial R)(R_0,\zeta)P(R_0,\zeta)$ obey $(\partial e_j/\partial R)(R_0,\zeta) = \lambda_j$, $j = 1,\ldots,d$. An analogous result holds for the ζ-derivative.*

Proof. Since the reasoning is the same for $\partial/\partial\zeta$ and $\partial/\partial R$, we only treat the latter case. The proof proceeds via the standard method of reducing the problem to finite-dimensional matrices acting on a fixed subspace. As explained in Ref. [37], it is possible to construct unitary and once-differentiable operators $U(R)$ with $U(R_0) = \mathbb{I}_{\mathcal{H}}$ and such that on a neighbourhood of R_0 the projections can be expressed as $P(R,\zeta) = U(R)P(R_0,\zeta)U(R)^{-1}$. Whence, $P(R,\zeta)h(R,\zeta)P(R,\zeta)$ is isospectral to the Hermitian matrix $P(R_0,\zeta)U(R)^{-1}h(R,\zeta)U(R)P(R_0,\zeta)$ acting on $P(R_0,\zeta)\mathcal{H}$. This matrix is differentiable with respect to R, and the derivatives of its eigenvalues are given by the eigenvalues of the derivative of the matrix (cf., Kato [37]). The formula for $\partial e/\partial R$ now follows from the observation that in $\big(\partial P(R_0,\zeta)U(R)^{-1}h(R,\zeta)U(R)P(R_0,\zeta)/\partial R\big)_{\upharpoonright R_0} = P(R_0,\zeta)(\partial h/\partial R)(R_0,\zeta)$ $P(R_0,\zeta)$ the derivatives of U^{-1} and U cancel at R_0.

Whereas for $\zeta < \sqrt{3}/4$ there are no problems with the operator $P(R_0,\zeta)$ $(\partial h/\partial R)(R_0,\zeta)P(R_0,\zeta)$ in the united atom situation $R_0 = 0$, if $\zeta \geq \sqrt{3}/4$ and $R_0 = 0$ the domain $\mathcal{D}\big(\partial h/\partial R\,(0,\zeta)\big)$ of the operator $\partial h/\partial R\,(0,\zeta)$ does not necessarily contain $\mathrm{Ran}\big(P(0,\zeta)\big)$ as subset. Nevertheless, even for $\psi \in \mathrm{Ran}\big(P(0,\zeta)\big)$ with $\psi \notin \mathcal{D}\big(\partial h/\partial R\,(0,\zeta)\big)$ the expression $\langle\psi,\, \partial h/\partial R\,(0,\zeta)\,\psi\rangle$ can be defined, e.g., by formulating it as a principal value integral around the singularity at $\boldsymbol{x} = 0$; then the principal value integral $\langle\psi,\, \partial h/\partial R\,(0,\zeta)\,\psi\rangle$

can be shown to vanish. On the other hand, from (i) of corollary 3.1 we know the vanishing of $\big(\partial e/\partial R\big)(0,\zeta)$. Hence, with such a definition of $\langle\psi,\, \partial h/\partial R\,(0,\zeta)\,\psi\rangle$, theorem 3.3 also holds for all $0<\zeta<1/2$ at $R_0=0$. ▌

4. BONDING AND STABILITY

4.1. The relativistic molecular virial theorem

For molecular Schrödinger operators containing multicentre Coulomb potentials, the virial theorem can be expressed as (see, e.g., [42])

$$\frac{\partial e_S}{\partial R}(R,\zeta) = -R^{-1}\big(e_S(R,\zeta)+\langle T_S\rangle\big) \tag{4.1}$$

where $e_S(R,\zeta)$ stands for an eigenvalue of the Schrödinger Hamiltonian and $\langle T_S\rangle$ denotes the expectation value of the kinetic energy operator $T_S=\boldsymbol{p}^2/2$ within the associated eigenfunction. To derive an analogue for the studied Dirac-Coulomb Hamiltonian, let $e_j(R,\zeta)$ be a nondegenerate eigenvalue of $h(R,\zeta)$ with eigenfunction $\psi_j(R,\zeta)$; in case of degeneracy, we assume a labeling chosen such that $e_j(R,\zeta)$ is differentiable in a neighbourhood of the considered R. Furthermore, let $\langle\beta\rangle_j=\langle\psi_j(R,\zeta),\,\beta\psi_j(R,\zeta)\rangle$. Then the virial theorem for $h(R,\zeta)$ reads:

Theorem 4.1. *For $0<\zeta<1/2$ and $R>0$, the R-derivative of the eigenvalue $e_j(R,\zeta)$ obeys*

$$\frac{\partial e_j}{\partial R}(R,\zeta) = -R^{-1}\big(e_j(R,\zeta)-\langle\beta\rangle_j\big). \tag{4.2}$$

Alternatively, we can equally express Eq. (4.2) in integrated form

$$e_j(R,\zeta) = R^{-1}\int_0^R \langle\beta\rangle_j\, ds \tag{4.3}$$

Since the proof of Eq. (4.2) consists of an easy application of the scaling properties discussed in section 2.2 and the second formula (4.3) follows from (4.2) by straightforward integration, we will skip the details here. In the limit $R\downarrow 0$, Eq. (4.3) reduces to the atomic version of the virial theorem for Dirac-Coulomb Hamiltonians, viz., $e_j(0,\zeta)=\langle\beta\rangle_j$ (cf. Ref. [26]). As for atomic systems, also for molecules we can invoke the virial theorem as a convenient tool to disprove the existence of eigenvalues embedded into the continuous part $(-\infty,-1]\cup[1,\infty)$ of the spectrum. The subsequent corollary is an immediate consequence of Eq. (4.3) and of the bound $-1\le\langle\psi,\,\beta\psi\rangle\le 1$ that holds for all normed $\psi\in\mathcal{H}$.

COROLLARY 4.1. *If $0 < \zeta < 1/2$ and $R \geq 0$, the eigenvalues $e_j(R,\zeta)$ of $h(R,\zeta)$ are bounded by*

$$-1 \leq e_j(R,\zeta) \leq 1 \tag{4.4}$$

Similar as in Schrödinger theory [47, 48, 49], a lower bound on the size of the molecule ensues as another off-spring from the virial theorem. More precisely, we can estimate R_e from below, where R_e marks the position of the (leftmost) minimum for a given PEC, i.e., the equilibrium separation for static nuclei within the given electronic state.

COROLLARY 4.2. *Let $0 < \zeta < \zeta_{\max}$ with $\zeta_{\max}$ from (2.38). For all electronic bound states the nuclear equilibrium positions R_e are bounded below by*

$$R_e \geq \alpha_S^{-1}\zeta^2\big(1-\sqrt{1-(2\zeta)^2}\big)^{-1}. \tag{4.5}$$

Proof. To derive the bound (4.5), we observe that the repulsive parts of the PECs are characterized by

$$\frac{\partial e_j}{\partial R}(R,\zeta) - \alpha_S^{-1}\zeta^2 R^{-2} \leq 0, \tag{4.6}$$

where for sufficiently small R the second term provides the leading contribution. Using Eq. (4.2) and, again, $\langle\beta\rangle_j \leq 1$ to estimate $\partial e_j/\partial R$ together with the UAL lower energy bound (2.41) leads to (4.5). ∎

The RHS of the inequality (4.5) is monotonically decaying in ζ from

$$R_e \geq \alpha_S^{-1}\big(\frac{1}{2} - \frac{1}{4}\zeta^2 + \mathcal{O}(\zeta^4)\big) \tag{4.7}$$

for small ζ, to $(4\alpha)^{-1}$ for $\zeta = 1/2$ (where we assume that the UAL lower bound can be extended to all $\zeta \in (0, 1/2)$). Comparison of (4.7) with the analogous bound for molecular Schrödinger operators [48] reveals that the latter is sharper by a factor of two; this is essentially a consequence of more efficient control of the term $\langle T_S\rangle$ within Schrödinger theory.

4.2. Stability properties

Within the Born-Oppenheimer approximation, a molecular system can be regarded as stable against dissociation if its ground state PEC enjoys a global minimum at some finite $0 < R_e < \infty$ (see, e.g., Refs. [47, 50, 51, 52, 53, 54] for a discussion of Schrödinger systems). This definition of stability is motivated by the observation that a global minimum of the PEC may accommodate bound vibrational levels, i.e., assuming sufficiently large (reduced) nuclear mass M and nonrelativistic kinematics for the vibrational motion of the nuclei, the operator $H_{\mathrm{vib}} = -(2M)^{-1}d^2/dR^2 + E(R)$ on the half-line $\mathbb{R}^+ \cup \{0\}$ with Dirichlet boundary conditions at $R = 0$ has (at least) one bound state. To compare the molecular ground state energies $E(R, \zeta) = e(R, \zeta) + \alpha_S^{-1}\zeta^2 R^{-1}$ with the the corresponding SAL energy $\lim_{R\to\infty} E(R, \zeta) = \lim_{R\to\infty} e(R, \zeta) = e^{\mathrm{at}}(\zeta)$, we may assume the positivity of $e(R, \zeta)$ and verify the existence of a global minimum by looking for some $0 < R < \infty$ with

$$\big(e(R, \zeta) + \alpha_S^{-1}\zeta^2 R^{-1}\big)^2 < e^{\mathrm{at}}(\zeta)^2. \tag{4.8}$$

As a consequence of the spectral theorem, $h(R, \zeta)^2 \geq e(R, \zeta)^2 \mathbb{I}_{\mathcal{H}}$; whence, by standard Rayleigh-Ritz variational arguments, the upper bound

$$\langle \psi,\, h(R,\, \zeta)^2 \psi\rangle \geq e(R, \zeta)^2 \tag{4.9}$$

for all $\psi \in \mathcal{D}(h(R, \zeta)^2)$ can be inferred. Therefore, setting

$$D(R, \zeta) = \langle \psi,\, \big(h(R,\, \zeta) + \alpha_S^{-1}\zeta^2 R^{-1}\big)^2 \psi\rangle - e^{\mathrm{at}}(\zeta)^2 \tag{4.10}$$

the inequality $D(R, \zeta) < 0$ for some $0 < R < \infty$ will guarantee the occurrence of a global minimum for the ground state PEC. With the notation $V_{\mathrm{ne}}^{\pm}$ from section 3.1 we can write $h(R, \zeta) = h^{\mathrm{at}}(R/2, \zeta) + V_{\mathrm{ne}}^{+}(R/2, \zeta)$. Since the application of $h(R, \zeta)^2$ onto the atomic ground state $\psi^{\mathrm{at}}(R/2, \zeta)$ is well-defined for the considered $0 < \zeta < 1/2$, and using $h(R, \zeta)\psi^{\mathrm{at}}(R/2, \zeta) = e^{\mathrm{at}}(\zeta)\psi^{\mathrm{at}}(R/2, \zeta) + V_{\mathrm{ne}}^{+}(R/2, \zeta)\psi^{\mathrm{at}}(R/2, \zeta)$, by choosing $\psi = \psi^{\mathrm{at}}(R/2, \zeta)$ as variational trial function we arrive at the following expression for $D(R, \zeta)$:

$$\begin{aligned} D(R,\, \zeta) = {} & 2\big(\langle \psi^{\mathrm{at}}(R/2, \zeta)\, V_{\mathrm{ne}}^{+}(R/2, \zeta)\psi^{\mathrm{at}}(R/2, \zeta)\rangle + \alpha_S^{-1}\zeta^2 R^{-1}\big)e^{\mathrm{at}}(\zeta) \\ & + \langle \psi^{\mathrm{at}}(R/2, \zeta),\, V_{\mathrm{ne}}^{+}(R/2, \zeta)^2 \psi^{\mathrm{at}}(R/2, \zeta)\rangle + 2\alpha_S^{-1}\zeta^2 R^{-1} \\ & \times \langle \psi^{\mathrm{at}}(R/2, \zeta),\, V_{\mathrm{ne}}^{+}(R/2, \zeta)\psi^{\mathrm{at}}(R/2, \zeta)\rangle + \alpha_S^{-2}\zeta^4 R^{-2} \end{aligned} \tag{4.11}$$

To decide on the sign of $D(R, \zeta)$, we need information about the integrals occurring in Eq. (4.11).

Lemma 4.1. *Consider $0 < \zeta < 1/2$. Then, with $\gamma = \sqrt{1 - \zeta^2}$, for R large*

$$\langle \psi^{\mathrm{at}}(R/2, \zeta),\, V_{\mathrm{ne}}^{+}(R/2, \zeta)\psi^{\mathrm{at}}(R/2, \zeta)\rangle = -\zeta R^{-1} + \mathcal{O}(R^{2\gamma-1}e^{-2\zeta R}) \tag{4.12}$$

and

$$\langle \psi^{\mathrm{at}}(R/2, \zeta),\, V_{\mathrm{ne}}^{+}(R/2, \zeta)^2 \psi^{\mathrm{at}}(R/2, \zeta)\rangle = \mathcal{O}(R^{-2}) \tag{4.13}$$

Proof. The conventional quantum numbers characterizing the (doubly degenerate) atomic ground state are $n = 1$, $j = 1/2$, $m_j = \pm 1/2$; choosing the plus sign for the latter, the explicit form for $\psi^{\mathrm{at}}(R/2, \zeta) = \tau_{R/2}\psi^{\mathrm{at}}(0, \zeta)$ is determined by

$$\psi^{\mathrm{at}}(0,\,\zeta)(\boldsymbol{r}) = \sqrt{\frac{\zeta^3(1+\gamma)}{\pi\Gamma(1+2\gamma)}}(2\zeta r)^{\gamma-1}e^{-\zeta r}\begin{pmatrix} 1 \\ 0 \\ i\zeta^{-1}(1-\gamma)\cos(\vartheta) \\ i\zeta^{-1}(1-\gamma)\sin(\vartheta)e^{i\varphi} \end{pmatrix} \tag{4.14}$$

with respect to usual radial coordinates r, ϑ, φ (see, e.g., [55]). Employing the abbreviations $r_\pm = |\boldsymbol{r} \pm \frac{1}{2}\boldsymbol{R}_s|$, the expectation value in Eq. (4.12) becomes

$$-\zeta \int d^3r\, r_+^{-1}|\psi^{\mathrm{at}}(0, \zeta)(\boldsymbol{r})|^2 = \frac{-\zeta \times (2\zeta)^{2\gamma+1}}{4\pi\Gamma(1+2\gamma)} I(R, \zeta). \tag{4.15}$$

To handle the integral

$$I(R, \zeta) = \int d^3r\, r_+^{-1} r_-^{2\gamma-2} e^{-2\zeta r_-}, \tag{4.16}$$

we introduce translated prolate spheroidal coordinates $\xi \in [0, \infty)$, $\eta \in [-2, 0)$, $\varphi \in [0, 2\pi)$, such that $r_+ = R(\xi + \eta + 2)/2$ and $r_- = R(\xi - \eta)/2$. Then I is cast into

$$I(R, \zeta) = 2^{-2\gamma+1}\pi R^{2\gamma}\int_0^\infty d\xi \int_{-2}^0 (\xi - \eta)^{2\gamma-1} e^{-\zeta R(\xi-\eta)}. \tag{4.17}$$

Although less obvious at first sight, for the analysis of the remaining two-dimensional integration it will be of advantage to set $\xi = \varrho\cos t$, $\eta = \varrho \sin t$ with $\varrho = \sqrt{\xi^2 + \eta^2}$, and to transform

$$I(R, \zeta) = 2^{-2\gamma+1}\pi R^{2\gamma}\int_{-\pi/2}^0 dt\, (\cos t - \sin t)^{2\gamma-1} F(t); \tag{4.18}$$

here,

$$F(t) = \int_0^{\varrho_b(t)} d\varrho\, \varrho^{2\gamma} e^{-c(t)\zeta R\varrho} \tag{4.19}$$

with $c(t) = \cos t - \sin t$, and with $\rho_b(t) = -2/\sin t$ marking the t-dependent upper integration limit, viz., the line $\eta = -2$. After these transformations, now it is straightforward to apply methods from Olver [56] (chapter 3.7, in particular) to identify the asymptotic behaviour of F and I. Since $1 \leq c(t)$ and $\rho_b(t) \geq 2$ for $t \in [-\pi/2, 0]$, the remainder in

$$F(t) = \big(c(t)\zeta R\big)^{-2\gamma-1}\Gamma(2\gamma+1) - \int_{\varrho_b(t)}^{\infty} d\varrho\, \varrho^{2\gamma} e^{-c(t)\zeta R\varrho} \tag{4.20}$$

is estimated by

$$\begin{aligned}\int_{\varrho_b(t)}^{\infty} d\varrho\, \varrho^{2\gamma} e^{-c(t)\zeta R\varrho} \leq & \int_{\varrho_b(t)}^{\infty} d\varrho\, \varrho^{2\gamma} e^{-\zeta R\varrho} = \\ &= (\zeta R)^{-2\gamma-1}\Gamma(2\gamma+1,\, \zeta\varrho_b(t)R) \\ &= \varrho_b(t)^{2\gamma}(\zeta R)^{-1} e^{-2\zeta\varrho_b(t)R}\big(1 + \mathcal{O}(1/(\zeta\varrho_b(t)R))\big) \\ &= \mathcal{O}(R^{-1}e^{-2\zeta R})\end{aligned} \tag{4.21}$$

uniformly in $t \in [-\pi/2, 0]$. Hence

$$\begin{aligned}I(R,\zeta) = 2^{-2\gamma+1}\pi\big(&\zeta^{-2\gamma-1}R^{-1}\Gamma(2\gamma+1)\int_{-\pi/2}^{0}(\cos t - \sin t)^{-2}\, dt \\ &+ \mathcal{O}(R^{-1+2\gamma}e^{-2\zeta R})\big) \\ = 4\pi(2\zeta)&^{-2\gamma-1}\Gamma(2\gamma+1)R^{-1} + \mathcal{O}(R^{-1+2\gamma}e^{-2\zeta R}),\end{aligned} \tag{4.22}$$

which yields Eq. (4.12).

Apart from unimportant factors, the expectation value in (4.13) involving $V_{\mathrm{ne}}^{+}(R,\zeta)^2$ is determined by an integral that in prolate spheroidals takes the form

$$\begin{aligned}I_{[-1,0]}(R,\zeta) + I_{[0,1]}(R,\zeta) = R^{2\gamma-1}\int_0^{\infty} d\xi\, \Big(&\int_{-1}^{0} d\eta\, (\xi+\eta)^{-1} \\ \times (\xi-\eta)^{2\gamma-1}e^{-\zeta R(\xi-\eta)} + &\int_0^1 d\eta\, (\xi+\eta)^{-1}(\xi-\eta)^{2\gamma-1}e^{-\zeta R(\xi-\eta)}\Big)\end{aligned} \tag{4.23}$$

where we have split the η-integration into the intervals $[-1, 0]$ and $[0, 1]$. For $I_{[0,1]}$, after translating $\xi \mapsto \xi - 1,\ \eta \mapsto \eta - 1$, we again set $\varrho = \sqrt{\xi^2 + \eta^2}$ and $\xi = \varrho\cos t,\ \eta = \varrho\sin t$. This leads to

$$I_{[0,1]}(R,\zeta) = R^{2\gamma-1}\int_{-\pi/2}^{0} dt\, c(t)^{2\gamma-1}\int_0^{\varrho_b(t)} Q_t(\varrho)e^{-c(t)\zeta R\varrho}\, d\varrho. \tag{4.24}$$

Here, $c(t)$ has the same meaning as before, whereas $\varrho_b(t) = -(\sin t)^{-1}$ describes the line $\eta = -1$, and $Q_t(\varrho) = \big(2 + \varrho(\cos t + \sin t)\big)^{-1}\varrho^{2\gamma}$. Since $2 + \varrho(\cos t + \sin t) \geq 1$ if $\varrho \in [0, \varrho_b(t)]$ and $t \in [-\pi/2, 0]$, for $\varrho \downarrow 0$ the behaviour

$Q_t(\varrho) \propto \varrho^{2\gamma}/2$ holds uniformly for all t in the considered interval. Hence we may invoke theorem 7.1 from Ref. [56] to conclude that the leading contribution to the ϱ-integral in (4.24) is given by $\frac{1}{2}\big(c(t)\zeta\big)^{-2\gamma-1}R^{-2\gamma-1}$, and therefore

$$I_{[0,1]}(R,\zeta) = R^{2\gamma-1}\mathcal{O}(R^{-2\gamma-1}) = \mathcal{O}(R^{-2}) \tag{4.25}$$

In case of $I_{[-1,0]}$, too, we adhere to the same sequence of transformations. First, we translate $\xi \mapsto \xi - 1$, $\eta \mapsto \eta + 1$, and then change to ρ, t variables. With the upper boundary $\varrho_b(t) = (\sin t)^{-1}$, we obtain

$$\begin{aligned} I_{[-1,0]}(R,\zeta) = R^{2\gamma-1}e^{-\zeta R}\int_0^{\pi/2} dt\,(\cos t + \sin t)^{-1}\int_0^{\varrho_b(t)} \big(2 + c(t)\varrho\big)^{2\gamma-1} \\ \times e^{-\zeta R(1+c(t)\varrho)}\,d\varrho \end{aligned} \tag{4.26}$$

where $1+c(t)\varrho \geq 0$ on the specified domain of integration. We now split the t-integral into two parts in accordance with the sign of $c(t)$. To this end, we choose $\kappa > 0$ such that $\rho_b(\frac{\pi}{4} - \kappa) < 2$ and decompose the integration interval $[0, \frac{\pi}{2}] = [0, \frac{\pi}{4} - \kappa] \cup [\frac{\pi}{4} - \kappa, \frac{\pi}{2}]$. Then $\varrho_b(t) < 2$ for $t \in [\frac{\pi}{4} - \kappa, \frac{\pi}{2}]$, whence for these t values the ρ-integration runs over a compact domain, and is easily estimated by a finite constant; thus

$$\begin{aligned} R^{2\gamma-1}e^{-\zeta R}\int_{\frac{\pi}{4}-\kappa}^{\pi/2} dt\,(\cos t + \sin t)^{-1}\int_0^{\varrho_b(t)} \big(2 + c(t)\varrho\big)^{2\gamma-1}e^{-\zeta R(1+c(t)\varrho)}\,d\varrho \\ \leq const \times R^{2\gamma-1}e^{-\zeta R}. \end{aligned} \tag{4.27}$$

For $t \in [0, \frac{\pi}{4} - \kappa]$, the function $c(t) > 0$ is nonnegative, which permits application of Olver's theorem 7.1 [56] to deduce $2^{\gamma-1}\Gamma(1)\big(\zeta R c(t)\big)^{-1}\exp(-\zeta R)$ as the leading asymptotics for the integral $\int_0^{\varrho_b(t)} Q_t(\varrho)\exp(-RP_t(\varrho))d\varrho$, where $Q_t(\varrho) = \big(2 + c(t)\varrho\big)^{2\gamma-1}$ and $P_t(\varrho) = \zeta(1 + c(t)\varrho)$. Since in addition $\int_0^{\pi/4-\kappa}\big((\cos t)^2 - (\sin t)^2\big)^{-1}dt < \infty$ is well-defined for $\kappa > 0$, we get

$$\begin{aligned} R^{2\gamma-1}e^{-\zeta R}\int_0^{\frac{\pi}{4}-\kappa} dt\,(\cos t + \sin t)^{-1}\int_0^{\varrho_b(t)} \big(2 + c(t)\varrho\big)^{2\gamma-1}e^{-\zeta R(1+c(t)\varrho}\,d\varrho \\ = \mathcal{O}\big(R^{2\gamma-2}e^{-2\zeta R}\big), \end{aligned} \tag{4.28}$$

which, together with (4.27) implies

$$I_{[-1,0]}(R,\zeta) = \mathcal{O}\big(R^{2\gamma-1}e^{-\zeta R}\big), \tag{4.29}$$

so that, eventually, the behaviour of $I_{[0,1]}$ in Eq. (4.23) dominates, and the asymptotics as stated in (4.13) results. ▮

Inserting the formulas from lemma 4.1 into Eq. (4.11) for the bound on the energy difference yields

$$D(R,\zeta) = 2\zeta e^{\mathrm{at}}(\zeta)(-1+\alpha_S^{-1}\zeta)R^{-1} + \mathcal{O}(R^{-2}). \tag{4.30}$$

Since $e^{\mathrm{at}}(\zeta) > 0$, then, as long as $Z = \alpha_S^{-1}\zeta < 1$, we infer $D(R,\zeta) < 0$ for R sufficiently large. This proves the first part of the following theorem.

THEOREM 4.2. *If $0 < Z = \alpha_S^{-1}\zeta < 1$, then the ground state PEC $E(R,\zeta)$ for the molecular system modeled by $H(R,\zeta) = h(R,\zeta) + V_{\mathrm{nn}}(R,\zeta)$ has a global minimum at some $0 < R_e < \infty$. If $Z = 1$, the ground state PEC for the hydrogen molecular ion H_2^+ has a global minimum for a finite R_e at least if $\alpha_S \in (0, 23/99]$ which includes the physical value of the fine structure constant $\alpha_S \approx 1/137$.*

Proof. Physically, our strategy above for $0 < Z < 1$ corresponds to attaching the electron to one of the nuclear centres and to observe that the other nucleus experiences a Coulomb attraction from the negative excess charge $Z-1$. If $Z = 1$, the excess charge vanishes, and terms of higher order than r^{-1} need to be studied. Rather than doing so, it appears easier to start from a modified variational trial function for $Z = 1$. Since relativistic corrections can be expected to play a minor role for the bonding of H_2^+, we replace our previous choice $\psi^{\mathrm{at}}(R/2,\zeta)$ by the "nonrelativistic" trial spinor

$$\psi(\boldsymbol{r}) = \begin{pmatrix} \phi(\boldsymbol{r})\chi_u \\ 0 \end{pmatrix} \tag{4.31}$$

where the lower ("small") components are assumed to vanish identically, and where the two-spinor χ_u is given by

$$\chi_u = Y_{00}\begin{pmatrix}1\\0\end{pmatrix} = \frac{1}{\sqrt{4\pi}}\begin{pmatrix}1\\0\end{pmatrix}. \tag{4.32}$$

The function ϕ is of LCAO type, i.e., we construct ϕ as the linear combination of hydrogenic ground state wave functions

$$\phi_{\mathrm{hyd}}(\boldsymbol{r}) = e^{-\alpha r} \tag{4.33}$$

translated to the two nuclear centres

$$\phi = \tau_{R/2}\phi_{\mathrm{hyd}} + \tau_{-R/2}\phi_{\mathrm{hyd}}. \tag{4.34}$$

While $\alpha > 0$ in (4.33) could be a more general variational parameter, here we demand it to be equal to α_S, and, in order to indicate that we do not consider α_S at a certain fixed value, below we shall suppress its subscript S. The matrix elements $\langle\psi, H^2\psi\rangle/\langle\psi,\psi\rangle$ computed with the ansatz (4.31) are listed in appendix B. In particular, using Eqs. (B.2), (B.4), (B.5), and $e^{\mathrm{at}}(\zeta)^2 = 1-\zeta^2$, the dissociation energy for ψ becomes

$$D(R,\zeta) = \zeta^2 + \tfrac{\langle\psi,-\Delta\psi\rangle}{\langle\psi,\psi\rangle} + 2\big(1+V_{\mathrm{nn}}(R,\zeta)\big)\tfrac{\langle\psi,V_{\mathrm{ne}}(R,\zeta)\psi\rangle}{\langle\psi,\psi\rangle} + \tfrac{\langle\psi,V_{\mathrm{ne}}(R,\zeta)^2\psi\rangle}{\langle\psi,\psi\rangle} + \big(2+V_{\mathrm{nn}}(R,\zeta)\big)V_{\mathrm{nn}}(R,\zeta). \tag{4.35}$$

We now specify to $\zeta=\alpha$, and, motivated by the equilibrium geometry encountered in nonrelativistic H_2^+ [53], we take $R=2/\alpha$ as a promising candidate for R_e. Furthermore, to employ the bound (B.14) on $\langle\psi,V_{\mathrm{ne}}^2\psi\rangle/\langle\psi,\psi\rangle$, we restrict α to the interval $0<\alpha\le 1/4$. Together, inserting also Eqs. (B.1), (B.3) and (B.4) into (4.35), we obtain

$$D(2/\alpha,\,\alpha) \;<\; \frac{\alpha^2 P(\alpha)}{1+\frac{13}{3}e^{-2}}, \tag{4.36}$$

where have estimated the coefficient of α^2 as

$$\frac{-\frac{5}{3}e^{-2}+2e^{-4}}{1+\frac{13}{3}e^{-2}} \;<\; \frac{-\frac{15}{88}}{1+\frac{13}{3}e^{-2}}, \tag{4.37}$$

and the coefficient of α^4 as

$$\frac{\frac{839}{276}-\frac{59}{12}e^{-2}+\frac{3}{2}e^{-4}}{1+\frac{13}{3}e^{-2}} \;<\; \frac{\frac{197}{82}}{1+\frac{13}{3}e^{-2}}, \tag{4.38}$$

and where we have set

$$P(\alpha) \;=\; -\tfrac{15}{88}+\tfrac{10}{59}\alpha+\tfrac{197}{82}\alpha^2+\tfrac{11}{112}\alpha^3. \tag{4.39}$$

Clearly, the polynomial $P(\alpha)$ is (strictly) monotonically increasing in $\alpha>0$, hence negativity of (4.36) for $0<\alpha\le 23/99 = 0.\overline{23}$ follows from

$$P(\tfrac{23}{99}) = -\tfrac{4223509}{23898287952}. \tag{4.40}$$

∎

To keep the analysis simple, we did not strive for optimal results when demonstrating stability for $Z=1$. Even with the "primitive" form (4.31) for ψ, a better adjustment of the variational parameter and of the equilibrium distance and sharper bounds would possibly yield a somewhat larger α_S-interval in theorem 4.2. We surmise that bonding in H_2^+ holds for all

$0 < \alpha_S < 1$. Nonetheless, similar as for the hydrogen atom where with an analogous trial function the ground state energy can be separated from the upper part of the continuous spectrum only if $\alpha_S < 1/\sqrt{2}$, for increasing α_S more sophisticated trial functions with relativistic ingredients will be required to obtain sufficiently tight variational bounds on the molecular energies. Since many of the arising molecular integrals will be difficult or impossible to express in closed form and the number of terms will proliferate rapidly, such calculations probably would not be tractable without relying heavily onto appropriate computer algebra methods and accepting computer assisted proofs.

In the nonrelativistic situation, numerical investigations [53] suggest that the critical charge Z_c until which a global minimum for the ground state PEC exists is given by $Z_c \approx 1.2367$; for nuclear charges $Z_c < Z < Z_m$ with $Z_m \approx 1.4391$ the PEC retains a local minimum above the SAL energy; this corresponds to a metastable regime for the system. If $Z > Z_m$, the PEC has a purely repulsive shape and the nuclear motion is unbound. For the Dirac-Coulomb Hamiltonian one would expect slightly larger values for analogously defined critical charges [57].

5. CONCLUDING REMARKS

In our investigations above, the motion of the nuclei has not been taken into account. To incorporate dynamical nuclei one can consider two possibilities. First, a fully relativistic model of the molecule encompassing also a relativistic treatment of the nuclei, i.e., using the Dirac kinetic energy $(2M)^{-1}\boldsymbol{\alpha}\cdot\boldsymbol{P}$ with $\boldsymbol{P} = -i\boldsymbol{\nabla}_{\boldsymbol{R}}$ for the nuclear motion. Whereas such a model would offer attractive consistency, apparently, however, rigorous results on a relativistic Born-Oppenheimer approximation or on relativistic molecular vibrations are still lacking in the literature (see, e.g., Ref. [58] for a rigorous nonrelativistic discussion). Alternatively, one may envisage a model with mixed kinematics for the molecule, where the electrons are described relativistically, but the nuclei in a nonrelativistic way, as motivated by the 10^3-10^4 times larger nuclear masses. Then, the electronic and nuclear motion can be separated via the conventional Born-Oppenheimer approximation such that the vibrational- or scattering-type trajectories of the nuclei are governed by a kinetic energy quadratic in the momentum plus an effective potential determined by the involved PECs.

It was mentioned in section 2.1 that in the UAL the essential self-adjointness of the Dirac-Coulomb Hamiltonian is lost if $\sqrt{3}/2 \leq 2\zeta < 1$, but a physically distinguished self-adjoint extension could be retained. That this particular – by atomic quantities identified – extension actually embodies the "authentic" one is also supported through the molecular context, viz., by the continuity of the electronic curves for $R \downarrow 0$ proved in section 3.1; any other choice of self-adjoint extension for the atomic operator should lead to a discontinuity of the electronic curves at $R = 0$. If for the molecular system $1/2 \leq \zeta < 1$, then the $R = 0$ operator $h(0, \zeta)$ carries a charge $2\zeta \geq 1$ excluding the physically distinguished self-adjoint extensions with finite kinetic or finite potential energy (the construction of self-adjoint operators in this regime is studied in Ref. [59]). Thus, the pathological behaviour of electronic curves with $\zeta \geq 1/2$ as $R \downarrow 0$ demonstrated by Klaus [19] should come as no surprise.

While our attention here has been restricted to homonuclear molecules, one of the next steps would be to examine heteronuclear systems by allowing different charges ζ_i attached to the nuclear centres. We expect appropriate generalizations of all our results to hold true also in those asymmetrical situations. On the other hand, since in sections 2.4 and 3.1 various proofs rely on the homonuclear symmetry, there is not much hope to extend their strategy to heteronuclear systems; so, novel ideas are called for. In case of the UAL bound for the molecular energies, we conjecture a particular molecular property to be valid that will imply the lower bound estimate (2.41) in theorem 2.4, namely the monotonic increase of the molecular ground state electronic curve, $e_0(R_1, \zeta) \leq e_0(R_2, \zeta)$ if $0 \leq R_1 \leq R_2$ (with ζ replaced by ζ_1, ζ_2 for heteronuclear molecules). Such a monotonicity has been indeed rigorously confirmed for Schrödinger Hamiltonians [60, 61, 62, 63], and for the (relativistic) Herbst operator [64] (where $(-\Delta + 1)^{1/2}$ serves as the kinetic energy part), and can be verified numerically for the Dirac-Coulomb Hamiltonian [57].

The least positively charged heteronuclear one-electron molecular ion would be HeH^{2+}; however, this species is far from being stable (cf., e.g., Ref. [53]). Hence, even an enhanced bonding in a relativistic model is certainly too weak to yield a bound dication HeH^{2+}. Our discussion of bonding in section 4.2 can be trivially extended to demonstrate that heteronuclear systems with charges $\zeta_1, \zeta_2 > 0$ are stable if $\max(\zeta_1, \zeta_2) \leq 1$. More realistic or sharper estimates for stability or instability of relativistic molecules still need to be found.

For multicentre systems with more than two nuclei, the available nuclear geometries increase rapidly and render the binding problem more complicated. Nonetheless, again the lack of stability of nonrelativistic $H_n^{(n-1)+}$ for $n > 2$ suggests instability of the relativistically described multicharged cations, too. In addition we expect multidimensional versions of our smoothness results for the electronic hypersurfaces to be valid.

APPENDIX A
Variational representation of Dirac energies

Here we give an outline of the variational principle for Dirac operators put forward by Dolbeault, Esteban, and Séré [23, 65]. Besides providing the reader with background material, the purpose of this appendix is also to point out a lower bound on the Dirac-Coulomb energies that can be deduced easily from their variational representation. The generalized minimax theorem as proved by Dolbeault, Esteban, and Séré in Ref. [23] reads as follows:

THEOREM A.1. *Let H be a self-adjoint operator with domain $\mathcal{D}(H) \subset \mathcal{H}$ with form domain $\mathcal{Q}(H)$. Let $\Gamma_\pm$ be orthogonal projections onto subspaces $\mathcal{H}_\pm \subset \mathcal{H}$ such that $\mathcal{H} = \mathcal{H}_+ \oplus \mathcal{H}_-$ Assume that there is a core $\mathcal{F}$ for H with*
(i) $\mathcal{F}_\pm$ are subspaces of $\mathcal{Q}(H)$, where $\mathcal{F}_\pm = \Gamma_\pm \mathcal{F}$
(ii) the action of H on $\mathcal{F}_-$ is bounded above in the sense that

$$a = \sup_{\phi \in \mathcal{F}_-,\, \phi \neq 0} \frac{\langle \phi, H\phi \rangle}{\langle \phi, \phi \rangle} < \infty \tag{A.1}$$

(iii) $\lambda_1 > a$, where for $k = 1, 2, \ldots$

$$\lambda_k = \inf_{\substack{\mathcal{V} \subset \mathcal{F}_+ \\ \dim \mathcal{V} = k}} \; \sup_{\substack{\psi \in \mathcal{V} \oplus \mathcal{F}_- \\ \psi \neq 0}} \frac{\langle \psi, H\psi \rangle}{\langle \psi, \psi \rangle} \tag{A.2}$$

and where the infimum runs over all subspaces of $\mathcal{F}_+$.
Then $\lambda_k = E_k$ for all eigenvalues $E_k \in (a, b)$, where $b = \inf\big((a, \infty) \cap \sigma_{\mathrm{ess}}(H)\big)$, or $\lambda_k = b$ if there is no E_k.

To facilitate the application of the preceding theorem to Dirac operators with potentials V, Dolbeault, Esteban, and Séré devised a "continuation principle"; its formulation below is adapted towards our studied atomic and molecular Dirac-Coulomb Hamiltonians and thus more specialized that the original version (theorem 3.1 in Ref. [23]).

THEOREM A.2. *Let T be a self-adjoint operator on $\mathcal{D}(T) \subset \mathcal{H}$. For a given bounded symmetric operator V, consider the one-parameter family $H(t) = T + tV$ with $0 \leq t \leq t_{\max}$, and such that each $H(t)$ obeys the assumptions (i) and (ii) of theorem A.1 with corresponding $a(t)$. In addition, we require that there exist $a_\pm$ such that $a(t) \leq a_- < a_+ \leq E_1(t)$ for all $t \in [0, t_{\max}]$, and that, for $t = 0$, the analogue of assumption (iii) in A.1 holds for $H(0) = T_D$, i.e., $\lambda_1(0) > a_-$. Then theorem A.1 is applicable to all $H(t)$ and their eigenvalues $E_k(t)$, $k = 1, 2, \ldots$ can be represented as $E_k(t) = \lambda_k(t) \geq a_+$ for $t \in [0, t_{\max}]$.*

Since the Coulomb terms $-\zeta|\boldsymbol{x} \pm \boldsymbol{R}/2|^{-1}$ are unbounded operators, they need to be regularized, e.g., by introducing $-\zeta\big(|\boldsymbol{x} \pm \boldsymbol{R}/2| + \varepsilon\big)^{-1}$ with $\varepsilon > 0$, before invoking theorem A.2; then, the results for the singular potential may be obtained via limiting arguments for $\varepsilon \downarrow 0$ (cf. section 4 of Ref. [23]).

The so-called Brown-Ravenhall or "no-pair" Hamiltonian h_{BR} is constructed to overcome instabilities arising from the negative energy continuum and associated unboundedness of the Dirac operator. By projecting onto the positive spectral subspace of the free Dirac Hamiltonian T_D with the projections $\theta_\pm$ from (2.23), one arrives at an operator

$$h_{\mathrm{BR}}(R,\zeta) = \theta_+ h(R,\zeta)\theta_+ \tag{A.3}$$

that, at least for not too large ζ, is semibounded from below. More precisely, strict positivity of the atomic Brown-Ravenhall energies of $h_{\mathrm{BR}}(0,2\zeta)$ can be demonstrated [66] if and only if $0 \le \zeta \le (\frac{\pi}{2} + \frac{2}{\pi})^{-1}$; for larger ζ, the operator $h_{\mathrm{BR}}(0,2\zeta)$ is no longer bounded from below [67]. For $R > 0$, the molecular energies are shown [68, 69] to be nonnegative if $0 \le \zeta \le 2/(\frac{\pi}{2} + \frac{2}{\pi}) \approx 0.9060$. In the atomic case, it is well-known [67, 66] that the Brown-Ravenhall energies provide lower bounds on the corresponding Dirac-Coulomb energies. Here, employing the variational principle above, we extend these bounds to the molecular situation.

THEOREM A.3. *Assume $0 < \zeta < (\frac{\pi}{2} + \frac{2}{\pi})^{-1}$, or, if $R > 0$, $0 < \zeta < 2/(\frac{\pi}{2} + \frac{2}{\pi})$. Then the eigenvalues $(e_{\mathrm{BR}})_k(R,\zeta)$ of $h_{\mathrm{BR}}(R,\zeta)$ are never larger than those of $h(R,\zeta)$,*

$$(e_{\mathrm{BR}})_k(R,\zeta) \le e_k(R,\zeta). \tag{A.4}$$

Proof. Since the prerequisites of theorem A.1 are satisfied (with $\theta_\pm$ being the projections onto the positive or negative, respectively, spectral spaces of T_D, and, e.g., $\mathcal{F} = C_0^\infty(\mathbb{R}^3, \mathbb{C}^4)$), we can use the formula (A.2) for the energies $e_k(R,\zeta)$ of $h(R,\zeta)$ as well as for the energies $(e_{\mathrm{BR}})_k(R,\zeta)$ of $h_{\mathrm{BR}}(R,\zeta)$. In the decomposition $\psi = \psi_+ \oplus \psi_-$ we choose $\psi_- = 0 \in \mathcal{F}_- = \theta_-\mathcal{F}$. Then $\langle\psi,\, h\psi\rangle = \langle\psi_+,\, h\psi_+\rangle = \langle\theta_+\psi,\, h\theta_+\psi\rangle = \langle\psi,\, h_{\mathrm{BR}}\psi\rangle$, and therefore the bound (A.4) turns out to be a consequence of the inequality

$$\sup_{\substack{\psi\in\mathcal{V}\oplus\mathcal{F}_-\\ \psi\neq 0}} \frac{\langle\psi,\, H\psi\rangle}{\langle\psi,\psi\rangle} \ge \sup_{\substack{\psi\in\mathcal{V}\oplus\{0\}\\ \psi\neq 0}} \frac{\langle\psi,\, H\psi\rangle}{\langle\psi,\psi\rangle}. \tag{A.5}$$

∎

Due to the semiboundedness of the Brown-Ravenhall Hamiltonian for $0 < \zeta \leq (\frac{\pi}{2} + \frac{2}{\pi})^{-1}$, we can apply standard Rayleigh-Ritz variational techniques to $h_{\mathrm{BR}}(R,\zeta) = \frac{1}{2}\theta_+ h^{\mathrm{at}}(-R/2,\, 2\zeta)\theta_+ + \frac{1}{2}\theta_+ h^{\mathrm{at}}(R/2,\, 2\zeta)\theta_+$ to conclude $e_{\mathrm{BR}}(R,\zeta) \geq e^{\mathrm{at}}_{\mathrm{BR}}(2\zeta)$ with $e^{\mathrm{at}}_{\mathrm{BR}}(2\zeta)$ standing for the ground state energy of the atomic Brown-Ravenhall Hamiltonian. Hence, as a consequence of theorem A.3, for ζ in this interval the atomic ground state energies $e^{\mathrm{at}}_{\mathrm{BR}}(2\zeta)$ may serve as lower bounds for the discrete spectrum of the atomic and molecular Dirac-Coulomb energies.

From the proof given above it should be clear that theorem A.3 can be extended to all potentials V for which the variational representation (A.2) for Dirac energies of $T_D + V$ holds, and for which simultaneously the eigenvalues of the corresponding Brown-Ravenhall Hamiltonian $\theta_+(T_D + V)\theta_+$ exist. In particular, if for $0 \leq t < 1$ one regards the family of operators $T_D + tV$ with potentials that satisfy $\sup_{\boldsymbol{x}\mathbb{R}^3}\big(|\boldsymbol{x}|V(\boldsymbol{x})\big) \leq 1$, upon showing that for sufficiently small $t > 0$ the associated Brown-Ravenhall ground state energies of $\theta_+(T_D + tV)\theta_+$ are nonnegative, our arguments from lemma 3.1 become applicable to rule out zero-energy eigenstates of $T_D + tV$ for all $0 < t < 1$. The continuity of the Dirac eigenvalues then prevents a change of their sign when t grows from smaller to larger values within the interval $(0,1)$. Hence the Hamiltonian $T_D + tV$ has no negative discrete spectrum if $t \in (0,1)$. In this way, an alternative and rather direct proof of theorem II.9 in Ref. [34] is achieved.

APPENDIX B
Matrix elements and bounds for $\langle \boldsymbol{H}^2 \rangle$

The simple ansatz (4.31) for the spinor ψ allows explicit calculation of most matrix elements in the variational expression for $\langle \psi,\, H(R,\zeta)^2\psi\rangle$. The remaining integrals in $\langle \psi,\, V_{\mathrm{ne}}(R,\zeta)^2\psi\rangle$ will be estimated by appropriate upper bounds. Below, we collect the matrix elements required in the proof of theorem 4.2, i.e., for the dissociation stability of H_2^+.

As for the nonrelativistic two-centre system, many of the arising integrals can be computed rather straightforwardly after changing to prolate spheroidal coordinates. In particular, for the norm $||\psi||^2$ of (4.31) we obtain

$$\langle \psi,\, \psi\rangle = \frac{1}{2\alpha^3}\Big(1 + (1 + \alpha R + \tfrac{1}{3}\alpha^2 R^2)e^{-\alpha R}\Big). \tag{B.1}$$

To determine $\langle \psi,\, T_D^2\psi\rangle$, we fall back onto the relation

$$T_D^2 = -\Delta + \mathbb{I} \tag{B.2}$$

and compute

$$\frac{\langle\psi,\,-\Delta\psi\rangle}{\langle\psi,\psi\rangle} = \alpha^2\,\frac{1+(1+\alpha R-\frac{1}{3}\alpha^2R^2)e^{-\alpha R}}{1+(1+\alpha R+\frac{1}{3}\alpha^2R^2)e^{-\alpha R}}. \tag{B.3}$$

Since in our ansatz for ψ the lower components vanish, while, on the other hand, the nontrivial results of the application of T_D reside in the lower components of $T_D\psi$, the expectation value of T_D just becomes

$$\langle\psi,\,T_D\psi\rangle = \langle\psi,\psi\rangle. \tag{B.4}$$

In the same way, it turns out that

$$\langle T_D\psi,\,V_{\rm ne}\psi\rangle = \langle\psi,\,V_{\rm ne}\psi\rangle. \tag{B.5}$$

The expectation value of $V_{\rm ne}(R,\zeta)$ is explicit,

$$\frac{\langle\psi,\,V_{\rm ne}\psi\rangle}{\langle\psi,\psi\rangle} = -\zeta\alpha\,\frac{1+(\alpha R)^{-1}\big(1-(1+\alpha R)e^{-2\alpha R}\big)+2(1+\alpha R)e^{-\alpha R}}{1+(1+\alpha R+\frac{1}{3}\alpha^2R^2)e^{-\alpha R}}, \tag{B.6}$$

whereas, unfortunately, not all integrals for of $V_{\rm ne}(R,\zeta)^2$ can be expressed in terms of elementary functions,

$$\begin{aligned}\frac{\langle\psi,\,V_{\rm ne}^2\psi\rangle}{\langle\psi,\psi\rangle} =& \frac{\zeta^2\alpha}{1+(1+\alpha R+\frac{1}{3}\alpha^2R^2)e^{-\alpha R}}\,\Big(\frac{\alpha^2}{R}\int_0^\infty dr\,re^{-2\alpha r}\ln\big(\frac{R+r}{R-r}\big)^2\\ &+4\alpha^2R\int_1^\infty d\xi\,\xi e^{-\alpha R\xi}\ln\big(\frac{\xi+1}{\xi-1}\big)\;+2\alpha+\frac{2}{R}\big(1-e^{-2\alpha R}\big)\Big).\end{aligned} \tag{B.7}$$

An upper bound on the first integral in Eq. (B.7) is derived by estimating (for $R\ge 1$)

$$\ln\Big(\frac{R+r}{R-r}\Big)^2 \;\le\; \begin{cases}\ln(2R-1)^2, & r\in[0,R-1]\\ \ln(2R)^2-\ln(R-r)^2, & r\in[R-1,R]\\ \ln(2R+1)^2-\ln(r-R)^2, & r\in[R,R+1]\\ \ln(2R+1)^2 & r\in[R+1,\infty),\end{cases} \tag{B.8}$$

which, together with similar estimates of the exponential function for $r\in[R-1,R]$ and $r\in[R,R+1]$, upon integration yields

$$\begin{aligned}\int_0^\infty dr\,re^{-2\alpha r}\ln\Big(\frac{R+r}{R-r}\Big)^2 \;\le\;& \frac{1}{4\alpha^2}\Big(\ln(2R-1)^2+(1-2\alpha+2\alpha R)\\ &\times e^{-2\alpha(R-1)}\ln\big(\tfrac{2R}{2R-1}\big)^2+(1+2\alpha R)e^{-2\alpha R}\ln\big(\tfrac{2R+1}{2R}\big)^2\Big)\\ &+(2R-\tfrac{1}{2})e^{-2\alpha(R-1)}+(2R+\tfrac{1}{2})e^{-2\alpha R}.\end{aligned} \tag{B.9}$$

The second integral in (B.7) can be bounded analogously,

$$\begin{aligned}\int_1^\infty d\xi\,\xi e^{-\alpha R\xi}\ln\Big(\frac{\xi+1}{\xi-1}\Big) \;&\leq\; e^{-\alpha R}\int_1^{4/3} d\xi\,\xi\ln\Big(\frac{\xi+1}{\xi-1}\Big) \\ &\qquad + \ln(7)\int_{4/3}^\infty d\xi\,\xi e^{-\alpha R\xi} \\ &= \Big(\tfrac{7}{18}\ln(7)+\tfrac{1}{3}\Big)e^{-\alpha R} + \ln(7)(\alpha R)^{-2}\Big(1+\tfrac{4}{3}\alpha R\Big)e^{-4\alpha R/3}.\end{aligned} \tag{B.10}$$

In the proof of theorem 4.2, we choose the internuclear separation R such that $\alpha R = 2$. Moreover, we only consider $\alpha \in (0, 1/4]$. Under these prerequisites, after inserting the inequalities (B.9) and (B.10) into (B.7), monotonicity arguments can be invoked to estimate further the terms that arise in the resulting bound on $\langle\psi, V_{\rm ne}^2\psi\rangle/\langle\psi,\psi\rangle$, viz.,

$$\frac{\alpha}{4}\ln\Big(\frac{4}{\alpha}-1\Big) \leq \Big[\frac{\alpha}{4}\ln\Big(\frac{4}{\alpha}-1\Big)\Big]_{\alpha=1/4} = \frac{\ln(15)}{16} < \frac{10}{59}, \tag{B.11}$$

and, with the following expression being regarded as coefficient of α,

$$\begin{aligned}&\tfrac{1}{4}(5-2\alpha)e^{-4+2\alpha}\ln\big(\tfrac{4}{4-\alpha}\big) + \tfrac{5}{4}e^{-4}\ln\big(\tfrac{4+\alpha}{4}\big) + 8\big((\tfrac{7}{18}\ln(7)+\tfrac{1}{3})e^{-2} \\ &\quad + \tfrac{11}{12}\ln(7)e^{-8/3}\big) + 3 - e^{-4} \;\leq\; \tfrac{5}{4}e^{-4+2\alpha}\ln\big(\tfrac{4}{4-\alpha}\big) + \tfrac{5}{4}e^{-4}\ln\big(\tfrac{4+\alpha}{4}\big) \\ &\qquad + 8\big((\tfrac{7}{18}\ln(7)+\tfrac{1}{3})e^{-2} + \tfrac{11}{12}\ln(7)e^{-8/3}\big) + 3 - e^{-4} \\ &\qquad\qquad \leq\; [\ldots]_{\alpha=1/4} \;<\; 3+\tfrac{89}{69},\end{aligned} \tag{B.12}$$

and correspondingly the coefficient of $\alpha^2/2$

$$\begin{aligned}(4-\tfrac{\alpha}{2})e^{-4+2\alpha} + (4+\tfrac{\alpha}{2})e^{-4} \;&\leq\; 4e^{-4+2\alpha} + (4+\tfrac{\alpha}{2})e^{-4} \\ &\leq\; [\ldots]_{\alpha=1/4} \;=\; 4e^{-7/2} + \tfrac{33}{8}e^{-4} \;<\; \tfrac{11}{56}.\end{aligned} \tag{B.13}$$

Combing the preceding inequalities (B.7-13), we arrive at a rather simple bound,

$$\frac{\langle\psi, V_{\rm ne}^2\psi\rangle}{\langle\psi,\psi\rangle} < \frac{\zeta^2\alpha}{1+\frac{13}{3}e^{-2}}\,\big(\tfrac{10}{59} + \tfrac{296}{69}\alpha + \tfrac{11}{112}\alpha^2\big), \tag{B.14}$$

valid for $\alpha R = 2$ and $0 < \alpha \leq 1/4$.

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