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ON THE STABILITY OF POSITIVE MOLECULAR IONS

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Abstract

Considering the nonrelativistic Schrödinger operator for homonuclear diatomic molecular ions within the clamped nuclei approximation, we study the stability problem for increasing ratio Z/N of nuclear charge Z to number N of electrons. In particular, we derive improved bounds on the critical parameters that imply instability (upper bounds on the nuclear charge, or, equivalently, lower bounds on the number of electrons), viz. parameters that lead to dissociation of the molecular system into atomic fragments. The principal qualitative advantange of our estimates is the inclusion of electronic correlation, i.e., taking into account the effect of electron-electron repulsion on the molecular bond. Comparing our rigorous results with empirical or computed data, we formulate a conjecture that should quantify the actual stability behaviour of realistic molecular species.

Key-Words : Schrödinger operator, diatomic molecular ions, stability.
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1. Introduction

Within the Born-Oppenheimer approximation, homonuclear diatomic molecular ions with N electrons are characterized by the Hamiltonian

$$H(R, Z, N) = h(R, Z, N) + Z^2/R \tag{1}$$

where $R > 0$ is the internuclear distance, $Z > 0$ the nuclear charge, and h is called the "electronic" Hamiltonian. To describe h, we fall back to the usual convention that the nuclei are lying on the z-axis (with unit vector $\hat{\mathbf{z}}$), and we denote the Coulomb interaction between the nuclei and the j-th electron by

$$-v(\mathbf{x}_j, R) := -v_+(\mathbf{x}_j, R) - v_-(\mathbf{x}_j, R) := -|\mathbf{x}_j + \tfrac{1}{2}R\hat{\mathbf{z}}|^{-1} - |\mathbf{x}_j - \tfrac{1}{2}R\hat{\mathbf{z}}|^{-1}. \tag{2}$$

Then, with the "noninteracting" Hamiltonian h^{ni} (i.e., h^{ni} does not take into account the interaction between electrons)

$$h^{\mathrm{ni}}(R, Z, N) := \sum_{j=1}^{N} h_j^{\mathrm{ni}}(R, Z) := \sum_{j=1}^{N} \Big(-\tfrac{1}{2}\Delta_j - Zv(\mathbf{x}_j, R)\Big), \tag{3}$$

the electronic Hamiltonian is specified by

$$h(R, Z, N) := h^{\mathrm{ni}}(R, Z, N) + \sum_{1 \le i < j \le N} |\mathbf{x}_i - \mathbf{x}_j|^{-1}. \tag{4}$$

Depending on whether bosonic or fermionic symmetry is considered, H and h are defined as self-adjoint operators on the symmetric or antisymmetric subspace of $\bigotimes(W^2(\mathbf{R}^3) \otimes \mathbf{C}^2)$ (W^2 stands for the second Sobolev space, and we are suppressing explicit spin-identity operators in the definitions (1-4), all operators acting trivially on the spin variables). If necessary, bosonic and fermionic quantities will be singled out by the superscript B or F, respectively. Otherwise, if no specification is given, the relevant statements will refer to both types of symmetry.

In this study, we will consider only the ground state and ground state energy of H or h. Employing the notation $\sigma(T)$ for the spectrum of the operator T, we define

$$\begin{aligned} E(R, Z, N) &:= \inf \sigma\big(H(R, Z, N)\big), \\ e(R, Z, N) &:= \inf \sigma\big(h(R, Z, N)\big) = E(R, Z, N) - Z^2/R. \end{aligned} \tag{5}$$

By convention, $R \mapsto E(R,Z,N)$ is called the ground state "potential energy curve" ("PEC"), and $R \mapsto e(R,Z,N)$ the ground state "electronic curve" for the molecular system characterized by the Hamiltonian (1). To describe the arising stability problems, let

$$E(Z,N) := \inf_{0<R<\infty} E(R,Z,N)$$

and suppose that the molecular species in its ground state enjoys an equilibrium configuration determined by the corresponding equilibrium nuclear separation R_e, i.e.

$$\exists\ 0 < R_e < \infty \qquad \text{such that} \qquad E(R_e,Z,N) = \inf_{0<R<\infty} E(R,Z,N). \tag{6}$$

For molecules, we have to distinguish two different kinds of stability:

Definition. *The ground state of the molecular system (1) is stable against*

(i) electron detachment ("autoionization") :$\Longleftrightarrow$ Eq. (6) does hold and $E(R_e,Z,N)$ is not within the essential spectrum of H,

$$E(R_e,Z,N) < \inf \sigma_{\text{ess}}\big(H(R_e,Z,N)\big) \tag{7}$$

(ii) molecular dissociation ("Coulomb explosion") :$\Longleftrightarrow$ Eq. (6) does hold and the ground state PEC has a genuine minimum,

$$E(R_e,Z,N) < \liminf_{R\to\infty}\ E(R,Z,N). \tag{8}$$

These definitions suggest corresponding critical parameters for Z or N that will bracket the associated stability intervals. In the case of the charge parameter Z, such critical values are introduced by

$$\begin{aligned} Z_{\text{ce}}(N) &:= \inf_{0<Z<\infty} \big\{Z \mid \text{Eq.s (6) and (7) hold for } Z \text{ and } N\big\} \\ Z_{\text{cd}}(N) &:= \sup_{0<Z<\infty} \big\{Z \mid \text{Eq.s (6) and (8) hold for } Z \text{ and } N\big\} \end{aligned} \tag{9}$$

and therefore $Z \in \big(Z_{\text{ce}}(N), Z_{\text{cd}}(N)\big)$ will imply a stable ground state of the N-electron molecular ion.

The electron detachment stability problem will not be considered further in this note, so below we will always assume Z, N such that $Z > Z_{\rm ce}(N)$ (for bounds on $Z_{\rm ce}$ cf. Ref. [1]). Our goal here is to study the function $Z_{\rm cd}$, i.e. to address the physical question " how many electrons are necessary to bind a molecule?". Obviously, the ratio

$$\mathcal{Z} := Z/N \tag{10}$$

is decisive for the stability behaviour. If $\mathcal{Z} \to 0$, the system will lose stability due to violation of (i), whereas for $\mathcal{Z} \to \infty$ the stability property (ii) will fail. In our analysis, attention will also be paid to the limit $Z_{\rm cd}(N)/N$ for $N \to \infty$. Moreover, from the beginning it should be clear that stability properties depend on the involved statistics, and that one may expect a higher stability for bosonic than for fermionic species, i.e., $Z^{\rm B}_{\rm cd}(N) \geq Z^{\rm F}_{\rm cd}(N)$.

Previous rigorous results on molecular type (ii) stability were first published by Ruskai [2] (without assuming the Born-Oppenheimer approximation). Explicit bounds on $Z_{\rm cd}(N)$ have been given by Duclos and Hogreve [3] and by Solovej [4]; the bound $Z_{\rm cd}(N) \leq 4N$ was obtained in Ref. [3] as a particular consequence of monotonicity of PECs, whereas the estimate $Z_{\rm cd}(N) \leq (1 + \sqrt{11/3}\,)N$ in Ref. [4] was derived by a different method (cf also below). Afterwards, Alarcón and Benguria [5], employing an improved lower bound on the equilibrium distance R_e, sharpened slightly the result by Solovej to $Z_{\rm cd}(N) \leq (1 + \sqrt{3})N$. On the other hand, numerical studies of these stability questions and computed critical charge values for specific molecular systems and various N between $N = 1$ and $N = 18$ can be found in Refs. [6-9].

2. Stability estimates

If $R \to \infty$, the molecular system will break up into two atomic ions, and the ground state PEC and electronic curve will obey

$$\liminf_{R\to\infty} E(R, Z, N) = \liminf_{R\to\infty} e(R, Z, N) = \min_{\alpha} E_{\alpha}(Z, N). \tag{11}$$

In Eq. (11), the minimum $\min_{\alpha}$ is taken over all decompositions $\alpha = (\alpha_1, \alpha_2)$ of the set of electrons $\{1, 2, \ldots, N\}$ into two clusters α_1, α_2, and $E_{\alpha} = E_{\alpha_1} + E_{\alpha_2}$ stand for the corresponding lowest energies, i.e., the infima of the respective spectra. By definition, stability of type (ii) requires existence of an equilibrium distance R_e and of an eigenfunction ϕ_e such that $H(R_e, Z, N)\phi_e = E(R_e, Z, N)\phi_e$. Moreover, due to condition (8), the molecular energy $E(R_e, Z, N)$ must be below the separated atoms energy

$$\langle \phi_e, H(R_e, Z, N)\phi_e\rangle - \min_{\alpha} E_{\alpha}(Z, N) < 0. \tag{12}$$

For a given cluster decomposition α, we denote the associated intercluster potential by

$$\begin{aligned} I_{\alpha}(R, Z) := &- Z \sum_{i\in\alpha_1} v_{-}(\mathbf{x}_i, R) - Z \sum_{j\in\alpha_2} v_{+}(\mathbf{x}_j, R) \\ &+ \sum_{i\in\alpha_1, j\in\alpha_2} |\mathbf{x}_i - \mathbf{x}_j|^{-1} + Z^2/R. \end{aligned} \tag{13}$$

Adopting the strategy of Ref. [4], by choosing (sufficiently smooth) functions $\chi_i : \mathbf{R}^3 \to \mathbf{R}_0^+$, $i = 1, 2$, with $\chi_1^2 + \chi_2^2 = 1$, a partition of unity on $\mathbf{R}^3$ associated with the decomposition α is defined by

$$J_{\alpha}(\mathbf{x}_1, \ldots, \mathbf{x}_N) := \prod_{i\in\alpha_1} \chi_1(\mathbf{x}_i) \prod_{j\in\alpha_2} \chi_2(\mathbf{x}_j). \tag{14}$$

Then, the expectation value of H can be estimated in the following way (for details see Ref. [4])

$$\begin{aligned} \langle \phi_e, H(R_e, Z, N)\phi_e\rangle \geq \sum_{\alpha} \{ &E_{\alpha}\langle \phi_e, J_{\alpha}^2 \phi_e\rangle + \langle \phi_e, J_{\alpha}^2 I_{\alpha}(R_e, Z, N)\phi_e\rangle \\ &- \langle \phi_e, \frac{1}{2}(\nabla J_{\alpha})^2 \phi_e\rangle \} \end{aligned} \tag{15}$$

where the last term in $\{\dots\}$ embodies the so-called "localization error". Combining inequalities (12) and (15), we arrive at a condition necessary for type (ii) stability:

$$\sum_{\alpha} \langle \phi_e, \left[J_\alpha^2 I_\alpha(R_e, Z, N) - \frac{1}{2}(\nabla J_\alpha)^2\right]\phi_e\rangle < 0. \tag{16}$$

This condition was first derived by Solovej, and also employed by Alarcón and Benguria in the same context. To exploit condition (16) for our purposes, we first note that (16) is certainly satisfied if the functions in $[\dots]$ are negative. Hence, after a scaling $\mathbf{x}_i \mapsto R_e \mathbf{x}_i$ (since the χ_i aren't yet specified explicitly, we continue to write χ_i for the localization functions in the scaled variables, too), sufficient for (16) is the pointwise inequality

$$-Z\sum_{i=1}^{N} V(\mathbf{x}_i) + \sum_{1\le i<j\le N} W(\mathbf{x}_i, \mathbf{x}_j) + Z^2 - (2R_e)^{-1}\sum_{i=1}^{N} \mathcal{E}(\mathbf{x}_i) < 0. \tag{17}$$

In (17), we employed the notation

$$\begin{aligned} V(\mathbf{x}) :=& \chi_1^2(\mathbf{x})v_-(\mathbf{x},1) + \chi_2^2(\mathbf{x})v_+(\mathbf{x},1) \\ W(\mathbf{x}_i,\mathbf{x}_j) :=& \left(\chi_1^2(\mathbf{x}_i)\chi_2^2(\mathbf{x}_j) + \chi_2^2(\mathbf{x}_i)\chi_1^2(\mathbf{x}_j)\right)/|\mathbf{x}_i - \mathbf{x}_j| \\ \mathcal{E}(\mathbf{x}) :=& \nabla\chi_1(\mathbf{x})^2 + \nabla\chi_2(\mathbf{x})^2 \end{aligned} \tag{18}$$

where the gradients $\nabla\chi_i$ reduce to the partial derivatives along the internuclear axis if the χ_i vary only along that direction.

Alternatively, if for some Z and all $R > 0$ the left hand side (LHS) of inequality (17) is pointwise nonnegative, this would entail failure of type (ii) stability for the N-electron molecule. A reformulation of (16) in that sense and more compact that (16) is obtained by applying the permutational (bosonic or fermionic) symmetry in the variables $\mathbf{x}_1, \dots, \mathbf{x}_N$. Doing so, and with $\mathcal{Z}$ defined as in Eq. (10) and $\mathcal{R} := 2NR$, the condition

$$-\mathcal{Z}^2 + V(\mathbf{x}_1)\mathcal{Z} - (2N)^{-1}(N-1)W(\mathbf{x}_1,\mathbf{x}_2) + \mathcal{R}^{-1}\mathcal{E}(\mathbf{x}_1) \le 0 \tag{19}$$

for all $\mathbf{x}_1, \mathbf{x}_2 \in \mathbf{R}^3$ and all $\mathcal{R} > 0$ implies violation of (16) and consequently instability for such Z/N-ratios. Furthermore, since $W(\mathbf{x}_1, \mathbf{x}_2) \ge 0$, omission of W provides an upper bound on the LHS of (19). Therefore, the simpler condition

$$-\mathcal{Z}^2 + V(\mathbf{x})\mathcal{Z} + \mathcal{R}^{-1}\mathcal{E}(\mathbf{x}) \le 0 \tag{20}$$

will determine (less sharp, of course) $\mathcal{Z}$-values that lead to instability. A straightforward application of conditions (19) or (20) is hampered by the fact that for $\mathcal{R} \to 0$ the last term $\mathcal{R}^{-1}\mathcal{E}$ becomes the dominant one, so that with $\mathcal{E}(\mathbf{x}) > 0$ this won't allow extraction of meaningful information on $\mathcal{Z}$ from these conditions. However, for (19) or (20) clearly it is not necessary to take into account those $\mathcal{R}$-ranges that cannot contain the possible $\mathcal{R}_e$ values. Thus, if $R_e^{\mathrm{LB}} \le R_e$ is a lower bound on the equilibrium separation R_e, and $\mathcal{R}_e^{\mathrm{LB}} := 2NR_e^{\mathrm{LB}}$, the $\mathcal{R}$-range for (19) or (20) can be restricted to $\mathcal{R}_e^{\mathrm{LB}} \le \mathcal{R} < \infty$. For instance, a simple lower bound of the form

$$\mathcal{R}_e \ge \mathcal{R}_e^{\mathrm{LB}} = 2 \tag{21}$$

for all $\mathcal{Z} > 0$, $N \ge 1$ will be established in the appendix (cf. part (i) of lemma 4).

Before we can apply conditions (19) or (20), we have to choose the localization functions χ_i. Here, we don't employ the χ_i proposed by Solovej [4,5], rather we fall back on functions that already have proven efficient for demonstrating the monotonicity of PECs in Ref. [3], and define

$$\begin{aligned} \chi_1(\mathbf{x}) &:= \begin{cases} 1, & \text{if } z \le -1/2; \\ \sqrt{(1+z)/2}(1-2z), & \text{if } -1/2 \le z \le 1/2; \\ 0, & \text{if } 1/2 \le z, \end{cases} \\ \chi_2(\mathbf{x}) &:= \chi_1(-\mathbf{x}) \end{aligned} \tag{22}$$

Evidently, these functions localize only with respect to variations along the internuclear axis $\hat{\mathbf{z}}$ and don't affect the orthogonal directions. Inserting the definitions (22) into Eq. (18), simple estimates yield

$$0 \le V(\mathbf{x}) \le \begin{cases} 2(1-2z^2) & \text{if } |z| < 1/2 \\ (1/2+|z|)^{-1} & \text{if } |z| \ge 1/2 \end{cases} \tag{23}$$

and

$$0 \le \mathcal{E}(\mathbf{x}) = \begin{cases} 9/(4(1-z^2)) & \text{if } |z| \le 1/2 \\ 0. & \text{if } |z| > 1/2 \end{cases} \tag{24}$$

Furthermore, the LHS of (20) can be bounded by

$$-\mathcal{Z}^2 + V(\mathbf{x})\mathcal{Z} + \mathcal{R}^{-1}\mathcal{E}(\mathbf{x}) \le -\mathcal{Z}^2 + \|V\mathcal{Z} + \mathcal{R}^{-1}\mathcal{E}\|_\infty \le -\mathcal{Z}^2 + \|V\|_\infty \mathcal{Z} + \mathcal{R}^{-1}\|\mathcal{E}\|_\infty . \tag{25}$$

Computing $||V||_\infty = 2$ and $||\mathcal{E}||_\infty = 3$, the last inequality of (25) leads to the condition

$$-\mathcal{Z}^2 + 2\mathcal{Z} + 3\mathcal{R}^{-1} \leq 0, \tag{26}$$

and, restricting $2 \leq \mathcal{R} < \infty$ in accordance with (21), the condition (26) is satisfied if

$$\mathcal{Z} \geq \tfrac{1}{2}\big(2 + \sqrt{10}\big) \approx 2.5811. \tag{27}$$

Alternatively, invoking the sharper first inequality in (24) together with the estimate

$$||V\mathcal{Z} + \mathcal{R}^{-1}\mathcal{E}||_\infty = \begin{cases} \mathcal{Z} + 3\mathcal{R}^{-1} & \text{if } \mathcal{R}\mathcal{Z} < 3/4 \\ 2\mathcal{Z} + 9/(4\mathcal{R}) & \text{if } \mathcal{R}\mathcal{Z} \geq 3/4, \end{cases} \tag{28}$$

the resulting condition

$$-\mathcal{Z}^2 + \max\{\mathcal{Z} + 3/\mathcal{R},\, 2\mathcal{Z} + 9/(4\mathcal{R})\} \leq 0 \tag{29}$$

for $2 \leq \mathcal{R} < \infty$ entails type (ii) instability if

$$\mathcal{Z} \geq \tfrac{1}{4}\big(4 + \sqrt{34}\big) \approx 2.4577. \tag{30}$$

To derive Eq. (28), just consider the function

$$m(z) = \begin{cases} 2(1 - 2z^2)\mathcal{Z} + 9/\big(4(1 - z^2)\mathcal{R}\big) & \text{if } |z| < 1/2 \\ \mathcal{Z}/\big(|z| + 1/2\big) & \text{if } |z| \geq 1/2. \end{cases} \tag{31}$$

The function m provides an upper bound on $V\mathcal{Z} + \mathcal{R}^{-1}\mathcal{E}$. If $\mathcal{R}\mathcal{Z} \leq 3/4$, then $||m||_\infty = \lim_{|z|\uparrow 1/2} m(z)$, whereas, if $\mathcal{R}\mathcal{Z} \geq 3/4$, the maximum of m is attained at $z = 0$.

We summarize the preceding results into

Theorem 1: *The relation (30) implies the upper bounds on the "stability function" $Z_{\rm cd}(N)$*

$$Z_{\rm cd}(N) \leq \tfrac{1}{4}\big(4 + \sqrt{34}\big)N. \tag{32}$$

Due to the nonnegativity of $\mathcal{E}$ (cf. Eq. (24)), the term $\mathcal{R}^{-1}\mathcal{E}$ representing the localization error is always monotonically increasing for decreasing $\mathcal{R}$, thus affecting the quality of the bounds (27) and (30) most strongly for $\mathcal{R} = \mathcal{R}_e^{\rm LB}$. Consequently, boosting the lower bound $\mathcal{R}_e^{\mathrm{LB}}$ will also improve the stability estimates above. As discussed in the appendix, sharper lower bounds $\mathcal{R}_e^{\mathrm{LB}}$ (in comparison to Eq. (21)) are implicitly determined by

$$4/\mathcal{R} + e_0(\mathcal{R}\mathcal{Z}/4) > 0 \tag{33}$$

and

$$\mathcal{R}_e^{\mathrm{LB}} = \sup_{\mathcal{R}>0}\{\mathcal{R} \mid \mathcal{R} \text{ obeys inequality (33)}\} \tag{34}$$

where $e_0(\lambda) \leq e(\lambda, 1, 1)$ is the ground state $N = 1$ electronic curve or a lower bound on it. The $\mathcal{Z}$-range for instability then follows from the system of two coupled inequalities, viz. either (26) or (29) in combination with (33). More precisely, setting $\lambda := \mathcal{Z}\mathcal{R}/4$ and $\tau := 4\mathcal{R}^{-1}$, those $\mathcal{Z}$-parameters with

$$\sup_{(\lambda,\tau)\in D_0}\{\lambda\tau\} \leq \mathcal{Z} \tag{35}$$

entrain type (ii) instability. The domain D_0 in (35) is given by

$$D_0 = \{(\lambda, \tau) \in \mathbf{R}^+ \times \mathbf{R}^+ \mid \tau \leq -e_0(\lambda) \quad \text{and} \quad \tau \leq \alpha_{-1}\lambda^{-1} + \alpha_{-2}\lambda^{-2}\} \tag{36}$$

where α_{-1}, α_{-2} are calculated from the coefficients of $\mathcal{Z}$ and $\mathcal{R}^{-1}$ in (26) or (29). Since $(\lambda, \tau) \mapsto \lambda\tau$ is a harmonic function, the supremum in (35) is attained at the boundary of D_0. In fact, if (λ_0, τ_0) denotes the crossing point of the two curves defining the boundary of D_0, it can be shown that $\sup_{(\lambda,\tau)\in D_0}\{\lambda\tau\} = \lambda_0\tau_0$. In this way, using (29) and for e_0 the lower bound function (A6) from the appendix, numerical computations yield $\mathcal{Z} \geq 2.3552$. If for e_0 the exact (numerical) electronic curve from Ref. [6] is employed, we end up with $\mathcal{Z} \geq 2.2673$ as instability implying condition.

3. Stability estimates including electronic correlation

In the previous section, all stability results were deduced by using the trivial upper bound $-W(\mathbf{x}_1, \mathbf{x}_2) \leq 0$ on the electron-electron repulsion term. Here now we will obtain sharper estimates on W in order to improve the stability bounds for $\mathcal{Z}$. Since $W(\mathbf{x}_1, \mathbf{x}_2) \to 0$ for $|\mathbf{x}_1 - \mathbf{x}_2| \to \infty$, it is clear that this goal can only be achieved if we succeed in constructing a partition of $\mathbf{R}^3 \times \mathbf{R}^3$ that allows to compensate opposite effects in the estimate of the $\mathbf{x}$-dependent terms in condition (19).

We start by observing that the rotational symmetry around the internuclear axis $\hat{\mathbf{z}}$ suggests a change to cylindrical coordinates (ρ, φ, z). Then, obviously, for all $\mathbf{x}_1, \mathbf{x}_2 \in \mathbf{R}^3$

$$|\mathbf{x}_1 - \mathbf{x}_2| \leq \sqrt{(z_1 - z_2)^2 + (\rho_1 + \rho_2)^2} \tag{37}$$

and thus

$$W(\mathbf{x}_1, \mathbf{x}_2) \geq W_a(z_1, z_2, \rho_1, \rho_2) := \chi_t^2(z_1, z_2)/\sqrt{(z_1 - z_2)^2 + (\rho_1 + \rho_2)^2} \tag{38}$$

where χ_t stands for the numerator in (18) with the choice (22) and expressed in z_1, z_2 variables

$$\chi_t^2(z_1, z_2) = \tfrac{1}{2} - \tfrac{9}{2} z_1 z_2 + 6(z_1^3 z_2 + z_1 z_2^3) - 8 z_1^3 z_2^3. \tag{39}$$

Employing permutational symmetry to rewrite (19) and applying the estimate (38), the function

$$F_1(z_1, z_2, \rho_1, \rho_2) := -\mathcal{Z}^2 + V_1(z_1, z_2, \rho_1, \rho_2)\mathcal{Z} - c_N W_a(z_1, z_2, \rho_1, \rho_2) + \mathcal{R}^{-1}\mathcal{E}_1(z_1, z_2) \tag{40}$$

with

$$\begin{aligned} V_1(z_1, z_2, \rho_1, \rho_2) :=& \big(V(\mathbf{x}_1) + V(\mathbf{x}_2)\big)/2 \\ \mathcal{E}_1(z_1, z_2) :=& \big(\mathcal{E}(z_1) + \mathcal{E}(z_2)\big)/2 \\ c_N :=& (N-1)/(2N) \end{aligned} \tag{41}$$

provides an upper bound on the LHS of (19). Therefore, we have the following condition for type (ii) instability

$$F_1(z_1, z_2, \rho_1, \rho_2) \leq 0 \tag{42}$$

(we don't indicate the dependence on the parameters $\mathcal{Z}, N$ and $\mathcal{R}$ in F_1). To analyze (42), we set $I := [-1/2, 1/2]$, $I^2 = I \times I$, $I_c^2 := \mathbf{R}^2 \setminus I^2$, $P_+ := \mathbf{R}_0^+ \times \mathbf{R}_0^+ := [0, \infty) \times [0, \infty)$, and we decompose the domain of F_1 as

$$\mathbf{R}^2 \times P_+ = I^2 \times P_+ \ \cup \ I_c^2 \times P_+. \tag{43}$$

First, we estimate F_1 on the "outer" region $I_c^2 \times P_+$ (i.e. at least one electron being not between the nuclear centres). Since on $I_c^2 \times P_+$ we have $|z_1| > 1/2$ or $|z_2| > 1/2$, an analysis analogous to the one employed in the derivation of Eq. (28) produces the following upper bound on F_1

$$F_1(z_1, z_2, \rho_1, \rho_2) \leq -\mathcal{Z}^2 + 3\mathcal{Z}/2 + 9/(8\mathcal{R}), \tag{44}$$

where we assumed (as we will do for the rest of this section) that $\mathcal{R}\mathcal{Z} \geq 3/4$.

To treat F_1 on the inner nuclear region $I^2 \times P_+$, we introduce a subdecomposition

$$I^2 \times P_+ = D_r \times P_+ \ \cup \ D_r^c \times P_+ \tag{45}$$

where

$$\begin{aligned} D_r :=& \{(z_1, z_2) \in \mathbf{R}^2 \mid z_1^2 + z_2^2 \leq r^2\} \\ D_r^c :=& I^2 \setminus D_r \end{aligned} \tag{46}$$

and $0 < r \leq 1/2$ is an adjustable (technical) parameter. Since $V(\mathbf{x}) = 2 - 4z^2$ for $\mathbf{x} = (0, 0, z)$ and $|z| \leq 1/2$, on the complement $D_r^c \times P_+$ to the inner disk the potential and localization error terms are bounded by

$$\begin{aligned} V_1(z_1, z_2, \rho_1, \rho_2) \leq& V_1(z_1, z_2, 0, 0) = (2 - 4z_1^2 + 2 - 4z_2^2)/2 \\ V_1(z_1, z_2, \rho_1, \rho_2)\mathcal{Z} + \mathcal{R}^{-1}\mathcal{E}_1(z_1, z_2) \leq& V_1(z_1, z_2, 0, 0)\mathcal{Z} + \mathcal{R}^{-1}\mathcal{E}_1(z_1, z_2) = f(z_1, z_2; \mathcal{Z}\mathcal{R})/\mathcal{R} \end{aligned} \tag{47}$$

where we have set

$$f(z_1, z_2; a) := 2(1 - z_1^2 - z_2^2)a + 9\big((1 - z_1^2)^{-1} + (1 - z_2^2)^{-1}\big)/8. \tag{48}$$

The function f can easily be shown to have no critical points within D_r^c if $r > 0$ and $a > 1$; hence, its suprema on D_r^c have to occur on the boundary, viz on the circle $z_1^2 + z_2^2 = r^2$

or on the line segments $\{(z_1, u) \mid |z_1| \leq 1/2\}$ or $\{(u, z_2) \mid |z_2| \leq 1/2\}$ for $u = \pm 1/2$. On the circle, the maximum of f is given by $2a(1-r^2) + 9(2-r^2)/(8(1-r^2))$, and, for $0 < r \leq 1/2$, $a > 1$, they are always greater than the maxima $3a/2 + 21/8$ on the line segments. Therefore, assuming $\mathcal{R}\mathcal{Z} > 1$, we have obtained as upper bound on F_1

$$F_1(z_1, z_2, \rho_1, \rho_2) \leq -\mathcal{Z}^2 + 2(1-r^2)\mathcal{Z} + \frac{9}{8\mathcal{R}} \times \frac{2 -. r^2}{1-r^2}. \tag{49}$$

It remains to examine F_1 on $D_r \times P_+$. Here, since $\left((z_1 - z_2)^2 + (\rho_1 + \rho_2)^2\right)^{1/2} \leq \left((z_1 - z_2)^2 + 2\rho_1^2 + 2\rho_2^2\right)^{1/2}$, we start with the bound

$$F_1(z_1, z_2, \rho_1, \rho_2) \leq F_2(z_1, z_2, \rho_1, \rho_2) \tag{50}$$

where

$$\begin{aligned} F_2(z_1, z_2, \rho_1, \rho_2) \quad := \quad -\mathcal{Z}^2 \quad + \\ \left\{ \frac{1}{\sqrt{1 + (2\rho_1)^2}} + \frac{1}{\sqrt{1 + (2\rho_2)^2}} - \frac{c_{N,\mathcal{Z}} \chi_t^2(z_1, z_2)}{\sqrt{2(z_1 - z_2)^2 + (2\rho_1)^2 + (2\rho_2)^2}} \right\} \mathcal{Z} + \mathcal{R}^{-1} \mathcal{E}_1(z_1, z_2) \end{aligned} \tag{51}$$

and

$$c_{N,\mathcal{Z}} := \frac{N-1}{\sqrt{2} N \mathcal{Z}}.$$

The bound (50) is a consequence of the following inequality

$$\frac{\chi_1^2(\mathbf{x}_i)}{\sqrt{(z_i - 1/2)^2 + \rho_i^2}} + \frac{\chi_2^2(\mathbf{x}_i)}{\sqrt{(z_i + 1/2)^2 + \rho_i^2}} \leq \frac{2}{\sqrt{1 + 4\rho_i^2}}$$

for $\mathbf{x}_i = (0, 0, z_i)$ and $i = 1, 2$, which in turn follows from the concavity of the mapping $u \mapsto u/\sqrt{u + 4\rho_i^2}$, $u \geq 0$, and the fact that $1 = (1/2)(1+z_i)(2z_i - 1)^2 + (1/2)(1-z_i)(2z_i+1)^2$; let us point out that this simple derivation of (50) depends crucially on particular properties unique to the choice (22) of the localization functions χ_i.

For an efficient treatment of F_2, we construct a (further) finer subdecomposition

$$D_r \times P_+ = \bigcup_{j=1}^{n} \Gamma_r^{(j)} \times P_+ \tag{52}$$

by introducing a partition of $[0, 2\pi]$

$$[0, 2\pi] = \bigcup_{j=1}^{n} [\theta_{j-1}, \theta_j] \tag{53}$$

$\theta_0 = 0$, $\theta_n = 2\pi$, $n \geq 1$, and setting

$$\Gamma_r^{(j)} := \{(z_1, z_2) \in D_r \mid \theta_{j-1} \leq \arctan(z_2/z_1) \leq \theta_j\}. \tag{54}$$

Actually, due to the invariance of F_2 under the mappings $(z_1, z_2) \mapsto (z_2, z_1)$ and $(z_1, z_2) \mapsto (-z_1, -z_2)$, it is sufficient to consider only a subpartition (covering a cone along the $+z_2$-axis) with

$$\tfrac{\pi}{4} = \theta_0 \leq \theta_{j-1} < \theta_j \leq \theta_n = \tfrac{3\pi}{4} \tag{55}$$

$j = 1, \ldots, n$. Then

$$F_2(z_1, z_2, \rho_1, \rho_2) \leq \max_{1 \leq j \leq n} \{ \sup_{(\rho_1, \rho_2) \in P_+} F_2^{(j)}(\rho_1, \rho_2)\} \tag{56}$$

where

$$\begin{aligned} F_2^{(j)}(\rho_1, \rho_2) &:= -\mathcal{Z}^2 + V_2\big((2\rho_1)^2, (2\rho_2)^2; a_j, b_j\big)\mathcal{Z} + \mathcal{R}^{-1}\varepsilon_j \\ V_2(s_1, s_2; a, b) &:= \frac{1}{\sqrt{1+s_1}} + \frac{1}{\sqrt{1+s_2}} - \frac{a^3}{\sqrt{b^2 + s_1 + s_2}} \end{aligned} \tag{57}$$

and where for all $z_1, z_2 \in \Gamma_r^{(j)}$

$$\begin{aligned} a_j &\leq \big(c_{N,\mathcal{Z}} \chi_t^2(z_1, z_2)\big)^{1/3} \\ b_j &\geq \big(2(z_1 - z_2)^2\big)^{1/2} \\ \varepsilon_j &\geq \mathcal{E}_1(z_1, z_2) \end{aligned} \tag{58}$$

are lower or upper bounds in the jth sector. Such bounds are best derived by using polar coordinates on D_r and monotonicity properties of the corresponding expressions. In this way, we get

$$\begin{aligned} a_j &= \Big(\tfrac{1}{4} c_{N,\mathcal{Z}} \big(2 + (-9r^2 + 12r^4 - 3r^6)\sin(2\theta_{j-1}) + r^6 \sin(6\theta_{j-1})\big)\Big)^{1/3} \\ b_j &= \sqrt{2} r |\sin(\theta_j) - \cos(\theta_j)|. \end{aligned} \tag{59}$$

Now, a reasonable compromise between sharpness and simplicity is achieved by the choice $n = 3$, $\theta_1 = \arcsin(\sqrt{35}/6)$, $\theta_2 = \pi - \theta_1$, leading to

$$\begin{aligned} a_1 =& \Big(c_{N,\mathcal{Z}}\big(\tfrac{1}{2} - \tfrac{9}{4}r^2 + 3r^4 - r^6\big)\Big)^{1/3} \\ a_2 =& \Big(c_{N,\mathcal{Z}}\big(\tfrac{1}{2} + \tfrac{\sqrt{35}}{2}\big(-\tfrac{1}{4}r^2 + \tfrac{1}{3}r^4 - \tfrac{35}{2916}r^6\big)\big)\Big)^{1/3} \\ a_3 =& \Big(c_{N,\mathcal{Z}}\big(\tfrac{1}{2} + \tfrac{\sqrt{35}}{2}\big(\tfrac{1}{4}r^2 - \tfrac{1}{3}r^4 + \tfrac{35}{2916}r^6\big)\big)\Big)^{1/3} \\ b_1 =& \tfrac{\sqrt{35}-1}{3\sqrt{2}}r \\ b_2 =& \tfrac{\sqrt{35}+1}{3\sqrt{2}}r \\ b_3 =& 2r. \end{aligned} \tag{60}$$

Similarly, applying monotonicity and the estimate $z_1^2 z_2^2 \geq r^4 \sin^2(\theta_1)\cos^2(\theta_1)$ on $\Gamma_r^{(1)}$ and $\Gamma_r^{(3)}$, we obtain

$$\begin{aligned} \varepsilon_1 =& \varepsilon_3 = \frac{9}{8} \times \frac{2 - r^2}{1 - r^2 + 35r^4/1296} \\ \varepsilon_2 =& \frac{9}{8} \times \frac{2 - r^2}{1 - r^2}. \end{aligned} \tag{61}$$

The proof of the following lemma is a simple exercise in calculus:

Lemma 2. *For given* $0 < a, b < 1$, *the function* $V_2(s_1, s_2; a, b)$ *on* P_+ *has as maximum*

$$\max_{s_1,s_2\geq 0} V_2(s_1, s_2; a, b) = \begin{cases} V_2(0, 0; a, b) = 2 - a^3/b & \text{if } a \leq b \\ V_2\big(\frac{a^2-b^2}{1-a^2}, 0; a, b\big) = 1 + \sqrt{\frac{(1-a^2)^3}{1-b^2}} & \text{if } a \geq b. \end{cases} \tag{62}$$

Moreover, the second maximum always bounds the first one

$$1 - \frac{a^3}{b} \leq \sqrt{\frac{(1 - a^2)^3}{1 - b^2}}. \tag{63}$$

Since we are assuming $\mathcal{Z} > 1$ (guaranteeing $a < 1$), we are allowed to invoke lemma 2 to estimate the supremum in inequality (56), thus arriving at

$$F_2(z_1, z_2, \rho_1, \rho_2) \leq -\mathcal{Z}^2 + \max_{1\leq j\leq 3} \Big\{\Big(1 + \sqrt{\frac{(1 - a_j^2)^3}{1 - b_j^2}}\Big)\mathcal{Z} + \mathcal{R}^{-1}\varepsilon_j\Big\}. \tag{64}$$

Up to now, we let $0 < r \leq 1/2$ as an open parameter. The final choice of r should render an optimal balance between contributions from D_r and from D_r^c. As it turns out, (approximately) optimal values for r depend on N. Being specific for the extreme cases $N = 2$ and $N \to \infty$, for $N = 2$ the choice $r = 4/15$ leads to

$$\begin{aligned} a_1^3 =& \frac{8083033}{2 \times 225^3} c_{2,\mathcal{Z}} \\ a_2^3 =& \left(\frac{1}{2} - \frac{13366154}{332150625}\sqrt{\frac{7}{5}}\right) c_{2,\mathcal{Z}} \\ a_3^3 =& \left(\frac{1}{2} + \frac{13366154}{332150625}\sqrt{\frac{7}{5}}\right) c_{2,\mathcal{Z}} \\ \varepsilon_1 =& \varepsilon_3 = \frac{7118685}{3047668}, \quad \varepsilon_2 = \frac{1953}{836} \end{aligned} \tag{65}$$

whereas in the situation $N \to \infty$ the slightly larger $r = 1/3$ yields

$$\begin{aligned} a_1^3 =& \frac{833}{2916} c_{\infty,\mathcal{Z}} \\ a_2^3 =& \left(\frac{1}{2} - \frac{6292\sqrt{35}}{531441}\right) c_{\infty,\mathcal{Z}} \\ a_3^3 =& \left(\frac{1}{2} + \frac{6292\sqrt{35}}{531441}\right) c_{\infty,\mathcal{Z}} \\ \varepsilon_1 =& \varepsilon_3 = \frac{13122}{5491}, \quad \varepsilon_2 = \frac{153}{64} \end{aligned} \tag{66}$$

with $c_{\infty,\mathcal{Z}} = (\sqrt{2}\mathcal{Z})^{-1}$. Eventually, after all these preparations, we are ready to formulate our main result.

Theorem 3. *If $\mathcal{Z} \geq 167/74 \approx 2.2568$, then for all $N \geq 2$ the molecular system described by the Hamiltonian (1) fails to be stable against dissociation (type (ii) instability), and the stability function Z_{cd} is bounded by*

$$Z_{\mathrm{cd}}(N) \leq 167N/74. \tag{67}$$

In the limit $N \to \infty$, the same holds true for $\mathcal{Z} \geq 123/56 \approx 2.1964$, and

$$\limsup_{N\to\infty} \big(Z_{\mathrm{cd}}(N)/N\big) \leq 123/56. \tag{68}$$

For the proof of theorem 3, we restrict the $\mathcal{R}$-range to be considered in conditions (44),(49), and (64) to $[13/5, \infty)$. This restriction is allowed by the monotonic decay of the ground state PEC for $\mathcal{R} \leq \mathcal{R}_e^{\mathrm{LB}} = 13/5$ and all $N \geq 1$, $\mathcal{Z} \geq 57/26$ (cf lemma 4 in the appendix). For $\mathcal{R} = \mathcal{R}_e^{\mathrm{LB}}$ (and thus for all $\mathcal{R} \geq \mathcal{R}_e^{\mathrm{LB}}$), it is easy to verify that the right hand sides (RHS) of (44), (49), and (64) are negative for $\mathcal{Z} = 167/74$, and, if $N \to \infty$, also for $\mathcal{Z} = 123/56$. The theorem then follows from the monotonic decay of (44), (49), (64) for increasing $\mathcal{Z}$. For the RHS of (44) or (49), the monotonicity in $\mathcal{Z}$ is obvious for $\mathcal{Z} \geq 3/2$ or $\mathcal{Z} \geq 1 \geq 1 - r^2$, respectively. In the case of condition (64), we set

$$g_j(\mathcal{Z}) := 1 + \sqrt{\frac{(1 - a_j(\mathcal{Z})^2)^3}{1 - b_j^2}} \tag{69}$$

and the nonpositivity of the $\mathcal{Z}$-derivative of the RHS of (64) is equivalent to

$$g_j(\mathcal{Z})\big(2 - \frac{dg_j}{d\mathcal{Z}}(\mathcal{Z})\big)^{-1} \leq \mathcal{Z}. \tag{70}$$

An immediate upper bound on $g_j(Z)$ is given by

$$g_j(\mathcal{Z}) \leq 1 + \frac{1}{\sqrt{1 - b_j^2}} \tag{71}$$

whereas, for $\mathcal{Z} \geq 1$, its derivative is estimated by

$$\frac{dg_j}{d\mathcal{Z}}(\mathcal{Z}) = \frac{a_j(\mathcal{Z})^2}{\mathcal{Z}} \sqrt{\frac{1 - a_j(\mathcal{Z})^2}{1 - b_j^2}} \leq \frac{a_j(1)^2}{\sqrt{1 - b_j^2}}. \tag{72}$$

Since for our chosen parameters r and all $j = 1, 2, 3$ we have $a_j(1)^2/\sqrt{1 - b_j^2} < 2$, the inequalities (71) and (72) determine a $\mathcal{Z}$-independent upper bound on the LHS of (70). Therefore, the condition (70) certainly holds if

$$\frac{\sqrt{1 - b_j^2} + 1}{2\sqrt{1 - b_j^2} - a_j(1)^2} \leq \mathcal{Z}, \tag{73}$$

and straightforward calculations confirm that (73) is satisfied for all $j = 1, 2, 3$ if $\mathcal{Z} \geq 19/10$, thus demonstrating the monotonicity of the RHS of (64) for such $\mathcal{Z}$ and completing the proof of theorem 3.

4. Concluding remarks

Focusing onto the dissociation stability problem for positive diatomic ions, in this study we derived bounds on the ratio of nuclear charge to the number of electrons decisive for molecular binding. This goal was accomplished by refining arguments of previous approaches and by devising and implementing certain correlation estimates that serve as a new tool within such a context. Along the various steps, the main quantitative improvement of about 15 % as compared to the original bound in Ref. [4] follows from applying better adapted localization functions. Employing sharper lower bounds on the equilibrium separation R_e, the result is further improved by approximately 4 %. Our principal qualitative innovation, the pointwise estimates of electronic correlation, leads to additional improvements between 3 % ($N = 2$) and 5 % ($N \to \infty$). Eventually, with all these ingredients, in total the obtained Z/N bounds are about 22 - 24 % below the result of Solovej [4]. Numerical experiments with condition (42) show that – if the analytical estimates from (42) towards (68) were optimal – an improvement up to approximately 35 % would be possible. Nonetheless, for the general situation, the condition (42) is not strong enough to yield bounds on $Z_{\mathrm{cd}}(N)$ that reach or drop below $2N$. The rather small influence of the electronic correlation on our $Z_{\mathrm{cd}}(N)$ bounds certainly falls short of its actual significance for the stability behaviour; on the other hand, however, the full contribution of the electron-electron interaction probably cannot be recovered without a detailed knowledge of the relevant wave functions.

A comparison with accurate computations on specific systems shows that the achieved rigorous bounds are not yet really sharp. For $N = 1$, the (numerically exact) critical charge $Z_{\mathrm{cd}}(1) = 1.2367$ from Ref. [6] implies the analogous result for the noninteracting Hamiltonian $H^{\mathrm{ni}}(R, Z, N) = h^{\mathrm{ni}}(R, Z, N) + Z^2/R$, viz $Z_{\mathrm{cd}}^{\mathrm{ni}}(N) = 1.2367N$. On physical grounds, since the electron-electron repulsion tends to weaken molecular bonding, one expects that the noninteracting case $Z_{\mathrm{cd}}^{\mathrm{ni}}(N)$ overestimates the true stability, $Z_{\mathrm{cd}}^{\mathrm{ni}}(N) \geq Z_{\mathrm{cd}}(N)$. This is confirmed by the computed value $Z_{\mathrm{cd}}(2) = 0.86 \times 2$ for $N = 2$ (cf Ref. [8]). For $N > 2$, distinction between bosonic and fermionic statistics will become significant. Experimentally, the existence of numerous metastable molecular ions X_2^{2+} has been established (see, e.g., the references in [6,8,9]). Stable doubly charged homonuclear species X_2^{2+}, however, have never been observed in experiment, or predicted by theoretical calculations, either. Thus, for realistic (i.e. fermionic) systems, one may conjecture

$$Z_{\mathrm{cd}}^{\mathrm{F}}(N) \leq N/2 + 1. \tag{77}$$

The bound (77) would be consistent with the asymptotic neutrality $Z_{\mathrm{cd}}^{\mathrm{F}}(N) \to N/2$ for $N \to \infty$, which was proved in Ref. [4]. For bosonic statistics, although no empirical data are available, neither the analogue of the conjecture (77) nor the corresponding asymptotic neutrality will remain true. Since neutral diatomic molecules are always bound by the attractive van-der-Waals force (as rigorously demonstrated by Lieb and Thirring [10]), it is clear that upper bounds on $Z_{\mathrm{cd}}(N)$ cannot be less that $N/2$.

There exist several perspectives how future investigations could produce sharper stability bounds. Apart from constructing superior localization functions and boosting further the lower bound on R_e, probably the most efficient and promising (but, on the other hand, difficult) route employs information on the involved ground state wave function ϕ. For such an approach, pointwise bounds on ϕ or bounds on some weighted averages of ϕ have to be established; then, they can be combined with the estimates used in this study to arrive at stronger stability conditions and thus at improved upper bounds on the Z/N-ratio.

Appendix: Lower bound on molecular equilibrium separation

For small internuclear separations, $R \downarrow 0$, in the Hamiltonian (1) the nuclear repulsion term Z^2/R will dominate the electronic part, so that – for sufficiently small R – PECs will decrease monotonically for increasing R. Obviously, as long as

$$\frac{\partial E}{\partial R}(R, Z, N) < 0, \tag{A1}$$

this will exclude existence of an equilibrium configuration and separation R_e (cf Eq.s (6) and (8)) for such R. Starting from (A1), it is not difficult to derive lower bounds R_e^{LB} on the equilibrium separation R_e [3,5,11]. Namely, with $\phi(R, Z, N)$ denoting the ground state of $H(R, Z, N)$, and, by using the molecular virial theorem [12] to evaluate $\partial E/\partial R$, a scaling argument to rewrite the resulting expression into an expectation value of $h(R/2, Z, N)$, and the variational principle to estimate it, the condition (A1) is certainly satisfied if we require negativity of the the upper bound

$$\begin{aligned}\frac{\partial E}{\partial R}(R, Z, N) &= -\frac{1}{2R}\langle\phi(R, Z, N), h(R/2, Z, N)\phi(R, Z, N)\rangle - \frac{Z^2}{R^2} \\ &\leq -\frac{1}{2R}e(R/2, Z, N) - \frac{Z^2}{R^2} < 0.\end{aligned} \tag{A2}$$

Since in (A2) the exact electronic energies are not known explicitely, rather than dealing with (A2) we have to content ourselves with a condition in which $e(R/2, Z, N)$ is replaced by lower bounds on it. From the definition (4) it is clear that $e^{\mathrm{ni}} \leq e$, where e^{ni} stands for the ground state electronic curve of the noninteracting Hamiltonian (3). Next, employing permutational symmetry (in $\mathbf{x}_1, \ldots, \mathbf{x}_N$) and scaling (in Z) properties, we obtain the chain of estimates

$$e(R/2, Z, N) \geq e^{\mathrm{ni}}(R/2, Z, N) \geq Ne(R/2, Z, 1) = NZ^2 e(\tfrac{RZ}{2}, 1, 1) \geq NZ^2 e^{\mathrm{LB}}(\tfrac{RZ}{2}). \tag{A3}$$

Here, e^{LB} is any lower bound function $u \mapsto e^{\mathrm{LB}}(u)$ on the electronic curve $u \mapsto e(u, 1, 1)$ of the H_2^+ molecular ion. The lower bounds R_e^{LB} used in the previous sections are consequences of the following lemma.

Lemma 4. *The ground state PEC $R \mapsto E(R,Z,N)$ for the Hamiltonian defined in (1) is monotonically decreasing in R*

(i) for all $R \le N^{-1}$ and $Z > 0$,

(ii) for all $R \le 13/(10N)$ and $Z \ge (57N)/26$.

The first part of lemma 4 follows immediately by combining (A1-A3) to infer

$$\frac{\partial E}{\partial R}(R,Z,N) \le -\frac{N^4\mathcal{Z}^2}{2\mathcal{R}}\, g(\mathcal{R},\mathcal{Z}) \tag{A4}$$

where

$$g(\mathcal{R},\mathcal{Z}) := \tfrac{4}{\mathcal{R}} + e^{\mathrm{LB}}\big(\tfrac{\mathcal{R}\mathcal{Z}}{4}\big), \tag{A5}$$

and by employing the trivial "united atom" lower bound $e^{\mathrm{LB}}(\mathcal{R}\mathcal{Z}/4) = -2$.

To prove part (ii), we have to resort to the more sophisticated lower bound function

$$e^{\mathrm{LB}}(u) = -\tfrac{5}{4} - \big(\tfrac{3}{4} + \tfrac{3}{2}u + u^2\big)\exp(-2u). \tag{A6}$$

This lower bound results from the operator inequality $h^{\mathrm{ni}}(u,1,1) \ge e_1^{\mathrm{hy}} \times \big(1 - P_0(u/2)\big) + e_0^{\mathrm{hy}} P_0(u/2) + e_1^{\mathrm{hy}} \times \big(1 - P_0(-u/2)\big) + e_0^{\mathrm{hy}} P_0(-u/2)$ and by solving the generalized 2×2-eigenvalue problem associated with its RHS (here, e_n^{hy} denotes the nth energy level of the hydrogen atom and $P_0(u)$ the projection onto its ground state centered at u; for details, see, e.g., Ref. [13]). Setting $\mathcal{R}_0 = 13/5$, $\mathcal{Z}_0 = 57/26$, it is easy to verify that

$$g(\mathcal{R}_0,\mathcal{Z}_0) > 0. \tag{A7}$$

For $\mathcal{Z} \ge \mathcal{Z}_0$, the inequality

$$g(\mathcal{R},\mathcal{Z}) \ge g(\mathcal{R}_0,\mathcal{Z}) \qquad \text{if} \qquad 0 < \mathcal{R} \le \mathcal{R}_0 \tag{A8}$$

follows from the monotonic decay

$$\frac{\partial g}{\partial \mathcal{R}}(\mathcal{R},\mathcal{Z}) = -\frac{4}{\mathcal{R}^2} + \frac{\mathcal{R}\mathcal{Z}^2}{16}\Big(1 + \frac{\mathcal{R}\mathcal{Z}}{2}\Big)\exp\Big(-\frac{\mathcal{R}\mathcal{Z}}{2}\Big) \le 0 \tag{A9}$$

which in turn follows from the fact that $8\mathcal{Z} \geq 8\mathcal{Z}_0 \geq t_m^3(1+t_m)\exp(-t_m) \geq t^3(1+t)\exp(-t)$ where $t := \mathcal{R}\mathcal{Z}/2$, and where the maximum of the function $t \mapsto t^3(1+t)\exp(-t)$ on $t \geq 0$ is attained at $t_m = (3+\sqrt{21})/2$. On the other hand, the monotonic increase

$$\frac{de^{\mathrm{LB}}}{du}(u) = u(1+2u)\exp(-2u) \tag{A10}$$

of e^{LB} implies that

$$g(\mathcal{R},\mathcal{Z}) \geq g(\mathcal{R},\mathcal{Z}_0) \qquad \text{if} \qquad \mathcal{Z} \geq \mathcal{Z}_0. \tag{A11}$$

Hence, the negativity of (A4) for $0 < \mathcal{R} \leq \mathcal{R}_0$ and $\mathcal{Z} \geq \mathcal{Z}_0$ is a consequence of (A7), (A8), and (A11).

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