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Rigorous energy bounds for two-electron systems

H. Hogreve

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Abstract Rigorous lower and upper bounds on the lowest three eigenvalues of the two-electron atomic Hamiltonian are obtained for the symmetry sectors $^1\mathrm{S}, ^3\mathrm{S}, ^1\mathrm{P}, ^3\mathrm{P}$ and the sector $^3\mathrm{P}^o$ with unnatural parity. The bounds result from three-dimensional projection operators and are given as explicit expressions that depend on the nuclear charge Z as parameter. They are designed for application within further analysis, and we exemplify this by demonstrating monotonicity properties of excitation energies.

Keywords Two-electron atom · Lower and upper bounds · Rigorous analysis · Excitation energies

1 Introduction

Lower boundedness is one of the essential properties of the standard nonrelativistic Schrödinger operators employed to describe atomic systems. As a consequence, (very) sharp upper bounds on discrete spectral points of these operators can be obtained by variational arguments, i.e., by invoking the minmax theorem [1,2]. By contrast, complementary lower bounds of comparable quality are much more difficult to acquire. For the simplest nontrivial situation, i.e., the helium atom, numerical upper bounds have been computed [4,5] that are believed to approximate the exact ground state energy up to more than 40 digits, while the sharpest lower bound [6] differs from this upper bound in the 14-th digit. From a quantitative point of view, these results are certainly completely sufficient to allow a definite comparison with experimental data

H. Hogreve (✉)
IFISR–International Foundation for Independent Scientific Research, 1133 Broadway Suite 706, New York, NY 10010, USA
e-mail: hogreve@ifisr.org; hogreve@rz.uni-hildesheim.de

or with, e.g., relativistic modifications of the theory. On the other hand, such results are of merely limited usefulness for an investigation of qualitative atomic properties. In particular, for studying the behaviour of atomic system and their characteristics when the nuclear charge Z is changed, not just numbers for a few selected Z but the explicit dependence of the bounds on the Z parameter will be of interest. Moreover, in this context also noninteger Z values are of relevance since by scaling and symmetry arguments energies of atoms with $N > 2$ electrons can be related to those of the two-electron system with scaled Z [3].

In the literature, various explicit expressions for rigorous lower (and upper) bounds on energy levels of the atomic two-electron system have been published [2,7,8]. Here we extend these results towards more states and increased accuracy. Optimal numerical results, however, are not the primary goal of our study, rather we strive for an appropriate balance between sharpness and simplicity of the bounds. Our emphasis on simplicity of the bounds is motivated by our aim to provide expressions that may serve as input for further analytical manipulations. An example revealing how the bounds derived in the subsequent Sect. 2 lead to rigorous qualitative properties of excitation energies will be discussed in Sect. 3. Atomic units are used throughout the paper.

2 Bounds from three-dimensional projections

Within standard nonrelativistic Schrödinger theory, atomic systems with two electrons are modeled by the Hamilton operator

$$H(Z) = H^{\mathrm{B}}(Z) + \frac{1}{r_{12}}, \quad H^{\mathrm{B}}(Z) = -\sum_{i=1}^{2}\left(\frac{1}{2}\Delta_i + \frac{Z}{|\mathbf{r}_i|}\right) \tag{1}$$

acting in the antisymmetrized tensor product space $\mathcal{H} = \bigwedge_{i=1}^{2} L^2(\mathbb{R}^3, \mathbb{C}^2) \cong \left(L^2(\mathbb{R}^3) \otimes \mathbb{C}^2\right) \otimes_A \left(L^2(\mathbb{R}^3) \otimes \mathbb{C}^2\right)$. Here $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ and we assume $Z > 0$ for the nuclear charge parameter Z. The operator H as well as its "base part" H^{B} are self-adjoint on $\bigwedge_{i=1}^{2} W^{2,2}(\mathbb{R}^3, \mathbb{C}^2)$ with $W^{k,p}$ standing for the usual Sobolev spaces [9]. Due to the commutation properties of the relevant operators, the eigenspaces of H and of H^{B} can be decomposed into the different symmetry sectors $^{2S+1}L^{\mathrm{e,o}}$ labeled by the quantum numbers for the total spin $2S+1$, the total angular momentum L, and by the parity $\mathcal{P}$ behaviour (where $\mathcal{P} = (-1)^L$ corresponds to "even" or "natural" and $\mathcal{P} = (-1)^{L+1}$ to "odd" or "unnatural" parity).

Lower bounds on spectral points of H can be derived by the method of intermediate operators [10], i.e., by using that

$$H(Z) \geq H^{\mathrm{LB}}(Z) = H^{\mathrm{B}}(Z) + r_{12}^{-1/2} P_K r_{12}^{-1/2} \tag{2}$$

for any projection operator P_K in $\mathcal{H}$. The particular choice [11,12]

$$P_K = \sum_{i,j=1}^{K} r_{12}^{1/2} |\psi_i^{\mathrm{B}}\rangle M_{ij} \langle \psi_j^{\mathrm{B}}| r_{12}^{1/2} \tag{3}$$

offers the advantage that the (symmetry adapted) eigenfunctions ψ_i^{B} of the base operator H^{B} are explicit and the matrix $W = ((W_{ij})) = ((\langle \psi_i^{\mathrm{B}}, r_{12}\psi_j^{\mathrm{B}}\rangle))$ and its inverse $M = W^{-1}$ can be computed in closed form. In fact, the ψ_i^{B} can be constructed as appropriate tensor products of hydrogenic functions $\psi_{n\ell m}(\mathbf{r}) = Y_\ell^m(\omega)\psi_{n\ell}^{\mathrm{rad}}(Zr)$ with $\mathbf{r} = (r, \omega)$ and the radial functions $\psi_{n\ell}^{\mathrm{rad}}(r) = (2/n^2)\sqrt{(n-\ell-1)!/(n+\ell)!}(2r/n)^\ell L_{n-\ell-1}^{2\ell+1}(2r/n)\exp(-r/n)$.

Obviously H^{LB} acts nontrivially only in a K dimensional subspace. Thus, the computation of its eigenvalues is reduced to determining the roots of a polynomial of degree K. While for $K = 1, 2$ this yields straightforward results [8], for $K = 3, 4$ the ensuing expressions become significantly more complicated. Nonetheless, in case of the characteristic polynomial associated with a symmetric (3,3) matrix, it is still possible to express the eigenvalues in a relatively compact way [13]; for H^{LB} they are of the form

$$\begin{aligned}
\mathcal{E}_1(Z) &= T(Z) + 2\sqrt{P(Z)} \cos\frac{1}{3}\left(2\pi + \arccos\frac{Q(Z)}{(P(Z))^{3/2}}\right) \\
\mathcal{E}_2(Z) &= T(Z) - \sqrt{P(Z)}\left(\cos\frac{1}{3}\arccos\frac{Q(Z)}{(P(Z))^{3/2}} - \sin\frac{1}{3}\arccos\frac{Q(Z)}{(P(Z))^{3/2}}\right) \\
\mathcal{E}_3(Z) &= T(Z) - 2\sqrt{P(Z)}\cos\frac{1}{3}\arccos\frac{Q(Z)}{(P(Z))^{3/2}}.
\end{aligned} \tag{4}$$

Here, $H_{ij}^{\mathrm{LB}} = \langle \psi_i^{\mathrm{B}}, H^{\mathrm{LB}}\psi_j^{\mathrm{B}}\rangle$ denote the matrix elements, $T = \mathrm{tr}((H_{ij}^{\mathrm{LB}}))/3$, and P, Q are polynomials in Z,

$$P(Z) = \frac{1}{6}\sum_{i,j=1}^{3}\left(H_{ij}^{\mathrm{LB}}(Z) - T(Z)\delta_{ij}\right)^2, \tag{5}$$

$$Q(Z) = \frac{1}{2}\det\left(\left(H_{ij}^{\mathrm{LB}}(Z) - T(Z)\delta_{ij}\right)\right). \tag{6}$$

Lower bounds on the eigenvalues $E_j(Z)$ of $H(Z)$ are then provided by

$$E_j^{\mathrm{LB}}(Z) = \min\left\{\mathcal{E}_j(Z), E_4^{\mathcal{B}}(Z)\right\} \le E_j(Z), \quad j = 1, 2, 3, \tag{7}$$

where $E_k^{\mathrm{B}}(Z)$ stands for the kth eigenvalue of the base operator $H^{\mathrm{B}}(Z)$. For the considered states, they are given by $E_k^{\mathrm{B}}(Z; {}^1\mathrm{S}) = -(1 + k^{-2})Z^2/2$ in the ${}^1\mathrm{S}$ sector, by $E_k^{\mathrm{B}}(Z; {}^3\mathrm{S}, {}^1\mathrm{P}, {}^3\mathrm{P}) = -(1 + (k+1)^{-2})Z^2/2$ in the sectors ${}^3\mathrm{S}, {}^1\mathrm{P}, {}^3\mathrm{P}$, and by $E_k^{\mathrm{B}}(Z; {}^3\mathrm{P}^{\mathrm{o}}) = -(1/4 + (k+1)^{-2})Z^2/2$ in the sector ${}^3\mathrm{P}^{\mathrm{o}}$ with unnatural parity.

Since the operator $H(Z)$ is bounded below, upper bounds on its eigenvalues complementary to the lower ones (7) can be produced from variational methods, e.g., by restricting $H(Z)$ to subspaces spanned by symmetry adapted ψ_i^{B}, $i = 1, \ldots, K$. If $K = 3$, the solutions $\tilde{\mathcal{E}}_i$ of the corresponding eigenvalue equations again are of the form (4) with P, Q replaced by the analogous quantities $\tilde{P}$, $\tilde{Q}$.

The base operator H^{B} being diagonal in the subspaces span$\{\psi_i^{\mathrm{B}}\}_{1\leq i\leq K}$, the interaction terms $\langle\psi_i^{\mathrm{B}}, r_{12}\psi_j^{\mathrm{B}}\rangle$ and $\langle\psi_i^{\mathrm{B}}, r_{12}^{-1}\psi_j^{\mathrm{B}}\rangle$ are the only nontrivial matrix elements. These matrix elements can be calculated exactly; due to a rapid proliferation of digits, however, their manual computation gets impractical already for low-lying excited states. On the other hand, with the help of computer algebraic systems (e.g., Mathematica, Reduce) the calculation of such matrix elements [14] as well as of all other quantities for the eigenvalues (4) for the lower and upper bounds no longer presents a problem. While the resulting expressions are exact and are not affected by numerical approximations, they may contain up to several hundred digits. Thus, to cast them into a form that can conveniently be used within an analytical context, we estimate the complicated expressions by simpler ones that involve not more than four or five digits. The simplified expressions $\mathcal{E}_i^{\mathrm{LB}}$ and $\mathcal{E}_i^{\mathrm{UB}}$ are built such that they still furnish rigorous bounds, i.e., $\mathcal{E}_i^{\mathrm{LB}} \leq \mathcal{E}_i$ and $\tilde{\mathcal{E}}_i \leq \mathcal{E}_i^{\mathrm{UB}}$, while at the same time not too much accuracy is lost, i.e., $\mathcal{E}_i^{\mathrm{LB}} \approx \mathcal{E}_i$ and $\mathcal{E}_i^{\mathrm{UB}} \approx \tilde{\mathcal{E}}_i$. More precisely, we estimate the coefficients in the polynomials $T(Z)$, $P(Z)$, $Q(Z)$ such that for all $Z \geq 0$

$$\begin{aligned} T^{\mathrm{L}}(Z) &= Z\left(t_0^{\mathrm{L}} - t_1^{\mathrm{L}} Z\right) \leq T(Z) = Z(t_0 - t_1 Z) \leq T^{\mathrm{U}}(Z) = Z\left(t_0^{\mathrm{U}} - t_1^{\mathrm{U}} Z\right) \\ Z^2 P^{\mathrm{L}}(Z) &= Z^2 \sum_{i=0}^{2} p_i^{\mathrm{L}}(-Z)^i \leq P(Z) = \sum_{i=2}^{4} p_i(-Z)^i \leq P^{\mathrm{U}} = Z^2 \sum_{i=0}^{2} p_i^{\mathrm{U}}(-Z)^i \\ Z^3 Q^{\mathrm{L}}(Z) &= Z^3 \sum_{i=0}^{3} q_i^{\mathrm{L}}(-Z)^i \leq Q(Z) = \sum_{i=3}^{6} q_i(-Z)^i \leq Q^{\mathrm{U}} = Z^3 \sum_{i=0}^{3} q_i^{\mathrm{U}}(-Z)^i \end{aligned} \tag{8}$$

and analogously for $\tilde{P}(Z)$ and $\tilde{Q}(Z)$. To deduce the wanted bounds on $\mathcal{E}_i$ and $\tilde{\mathcal{E}}_i$ from these estimates, we need the following simple monotonicity properties.

Lemma 2.1 *The functions* $x \mapsto f_1(x) = \cos\frac{1}{3}(2\pi + \arccos x)$ *and* $x \mapsto f_2(x) = \cos\frac{1}{3}\arccos x - \sqrt{3}\sin\frac{1}{3}\arccos x$ *are monotonically increasing while* $x \mapsto f_3(x) = \cos\frac{1}{3}\arccos x$ *is monotonically decreasing for* $x \in [-1, 1]$.

Proof Since $\frac{1}{3}\arccos x \in [0, \pi/3]$ for $-1 \leq x \leq 1$, the nonnegativity of the derivative f_1' follows from $\sin y \geq 0$ for $2\pi/3 \leq y \leq \pi$, and, after writing $f_2(x) = f_1(x) + \sqrt{3}\sin\frac{1}{3}(2\pi + \arccos x)$, the nonnegativity of f_2' results by using that also $-\cos y \geq 0$ if $2\pi/3 \leq y \leq \pi$. On the other hand, the nonpositivity of f_3' is a consequence of $-\sin y \leq 0$ for $0 \leq y \leq \pi/3$. □

The polynomials $Q^{\mathrm{L,U}}(Z)$ and $\tilde{Q}^{\mathrm{L,U}}(Z)$ obey $Q^{\mathrm{L,U}}(0) > 0$ and $\tilde{Q}^{\mathrm{L,U}}(0) > 0$ and enjoy only one (nonnegative) real root $Z_0^{\mathrm{L,U}}$, $\tilde{Z}_0^{\mathrm{L,U}}$, respectively. Hence $Q^{\mathrm{L,U}}(Z) > 0$ if $0 \leq Z < Z_0^{\mathrm{L,U}}$ while $Q^{\mathrm{L,U}}(Z) < 0$ if $0 \leq Z > Z_0^{\mathrm{L,U}}$, and analogously for

$\tilde{Q}^{\mathrm{L,U}}$. In the subsequent theorem therefore we have to distinguish between these two Z domains.

Theorem 2.1 *Let $E_i(Z)$, $i = 1, 2, 3$, be the lowest energies of $H(Z)$ within a specified symmetry sector (i.e., $E_1(Z) = \inf\{\sigma(H(Z))\}$ and $E_j(Z) = \inf\{\sigma(H(Z)) \setminus E_{j-1}(Z)\}$, $j > 1$, where $\sigma(H)$ denotes the spectrum of H). Then for $Z > 0$*

$$\min\left\{E_i^{\mathrm{LB}}(Z), E_4^{\mathrm{B}}(Z)\right\} \leq E_i(Z) \leq \min\left\{E_i^{\mathrm{UB}}(Z), E_\infty(Z)\right\} \tag{9}$$

where

$$E_1^{\mathrm{LB}}(Z) = T^{\mathrm{L}} + 2Z\sqrt{P^{\mathrm{U}}(Z)}\cos\frac{1}{3}\left(2\pi + \arccos\frac{Q^{\mathrm{L}}(Z)}{(P_1(Z))^{3/2}}\right)$$

$$E_2^{\mathrm{LB}}(Z) = T^{\mathrm{L}} - Z\sqrt{P^{\mathrm{L}}(Z)}\left(\cos\frac{1}{3}\arccos\frac{Q^{\mathrm{U}}(Z)}{(P_2(Z))^{3/2}} - \sqrt{3}\sin\frac{1}{3}\arccos\frac{Q^{\mathrm{U}}(Z)}{(P_2(Z))^{3/2}}\right)$$

$$E_3^{\mathrm{LB}}(Z) = T^{\mathrm{L}} - 2Z\sqrt{P^{\mathrm{L}}(Z)}\cos\frac{1}{3}\arccos\frac{Q^{\mathrm{L}}(Z)}{(P_3(Z))^{3/2}}$$

$$E_1^{\mathrm{UB}}(Z) = T^{\mathrm{U}} + 2Z\sqrt{\tilde{P}^{\mathrm{L}}(Z)}\cos\frac{1}{3}\left(2\pi + \arccos\frac{\tilde{Q}^{\mathrm{U}}(Z)}{(\tilde{P}_1(Z))^{3/2}}\right)$$

$$E_2^{\mathrm{UB}}(Z) = T^{\mathrm{U}} - Z\sqrt{\tilde{P}^{\mathrm{U}}(Z)}\left(\cos\frac{1}{3}\arccos\frac{\tilde{Q}^{\mathrm{L}}(Z)}{(\tilde{P}_2(Z))^{3/2}} - \sqrt{3}\sin\frac{1}{3}\arccos\frac{\tilde{Q}^{\mathrm{L}}(Z)}{(\tilde{P}_2(Z))^{3/2}}\right)$$

$$E_3^{\mathrm{UB}}(Z) = T^{\mathrm{U}} - 2Z\sqrt{\tilde{P}^{\mathrm{U}}(Z)}\cos\frac{1}{3}\arccos\frac{\tilde{Q}^{\mathrm{U}}(Z)}{(\tilde{P}_3(Z))^{3/2}} \tag{10}$$

and

$$P_1(Z) = \begin{cases} P^{\mathrm{U}}(Z), & Z < Z_0^{\mathrm{L}} \\ P^{\mathrm{L}}(Z), & Z \geq Z_0^{\mathrm{L}} \end{cases} \qquad \tilde{P}_1(Z) = \begin{cases} \tilde{P}^{\mathrm{L}}(Z), & Z < \tilde{Z}_0^{\mathrm{U}} \\ \tilde{P}^{\mathrm{U}}(Z), & Z \geq \tilde{Z}_0^{\mathrm{U}} \end{cases}$$

$$P_2(Z) = \begin{cases} P^{\mathrm{L}}(Z), & Z < Z_0^{\mathrm{U}} \\ P^{\mathrm{U}}(Z), & Z \geq Z_0^{\mathrm{U}} \end{cases} \qquad \tilde{P}_2(Z) = \begin{cases} \tilde{P}^{\mathrm{U}}(Z), & Z < \tilde{Z}_0^{\mathrm{L}} \\ \tilde{P}^{\mathrm{L}}(Z), & Z \geq \tilde{Z}_0^{\mathrm{L}} \end{cases} \tag{11}$$

$$P_3(Z) = \begin{cases} P^{\mathrm{U}}(Z), & Z < Z_0^{\mathrm{L}} \\ P^{\mathrm{L}}(Z), & Z \geq Z_0^{\mathrm{L}} \end{cases} \qquad \tilde{P}_3(Z) = \begin{cases} \tilde{P}^{\mathrm{L}}(Z), & Z < \tilde{Z}_0^{\mathrm{U}} \\ \tilde{P}^{\mathrm{U}}(Z), & Z \geq \tilde{Z}_0^{\mathrm{U}} \end{cases}$$

The coefficients for the $T^{\mathrm{L,U}}$, $Q^{\mathrm{L,U}}$, $P^{\mathrm{L,U}}$, $\tilde{Q}^{\mathrm{L,U}}$, $\tilde{P}^{\mathrm{L,U}}$ and the symmetry sectors $^1\mathrm{S}, {}^3\mathrm{S}, {}^1\mathrm{P}, {}^3\mathrm{P}, {}^3\mathrm{P^o}$ are collected in Tables 1 *and* 2. *Furthermore, in* Table 3 *we present bounds for the roots $Z_0^{\mathrm{L,U}}$, $\tilde{Z}_0^{\mathrm{L,U}}$ and for the crossings between $E_i^{\mathrm{LB}}(Z)$ and $E_4^{\mathrm{B}}(Z)$. The threshold E_∞ of the continuous spectrum is determined by $E_\infty(Z) = -Z^2/2$ for the even partity states, and by $E_\infty(Z) = -Z^2/8$ in the $^3\mathrm{P^o}$ symmetry sector.*

Table 1 Coefficients of the lower bound polynomials T^{L}, $Q^{\mathrm{L,U}}$, and $P^{\mathrm{L,U}}$

	^{1}S		^{3}S		^{1}P		^{3}P		^{3}P$^{\mathrm{o}}$	
	T^{L}		T^{L}		T^{L}		T^{L}		T^{L}	
t_0^{L}	$\frac{700}{963}$		$\frac{712}{2439}$		$\frac{1783}{5183}$		$\frac{2725}{8279}$		$\frac{3989}{15049}$	
t_1^{L}	$\frac{157}{72}$		$\frac{493}{288}$		$\frac{493}{288}$		$\frac{493}{288}$		$\frac{169}{288}$	
	P^{L}	P^{U}	P^{L}	P^{U}	P^{L}	P^{U}	P^{L}	P^{U}	P^{L}	P^{U}
$p_0^{\mathrm{L,U}}$	$\frac{131}{8409}$	$\frac{21}{1348}$	$\frac{32}{19605}$	$\frac{26}{15929}$	$\frac{55}{19187}$	$\frac{41}{14303}$	$\frac{3}{1261}$	$\frac{28}{11769}$	$\frac{15}{15638}$	$\frac{40}{41701}$
$p_1^{\mathrm{L,U}}$	$\frac{1118}{33987}$	$\frac{1178}{35811}$	$\frac{81}{39292}$	$\frac{23}{11157}$	$\frac{3}{1096}$	$\frac{74}{27035}$	$\frac{3}{1195}$	$\frac{77}{30672}$	$\frac{28}{17529}$	$\frac{27}{16903}$
$p_2^{\mathrm{L,U}}$	$\frac{889}{46656}$	$\frac{889}{46656}$	$\frac{5}{6337}$	$\frac{38}{48161}$	$\frac{5}{6337}$	$\frac{38}{48161}$	$\frac{5}{6337}$	$\frac{38}{48161}$	$\frac{5}{6337}$	$\frac{38}{48161}$
	Q^{L}	Q^{U}	Q^{L}	Q^{U}	Q^{L}	Q^{U}	Q^{L}	Q^{U}	Q^{L}	Q^{U}
$q_0^{\mathrm{L,U}}$	$\frac{333}{222446}$	$\frac{173}{115565}$	$\frac{1}{22178}$	$\frac{1}{22173}$	$\frac{3}{25483}$	$\frac{1}{8494}$	$\frac{3}{35812}$	$\frac{1}{11937}$	$\frac{1}{71079}$	$\frac{1}{70578}$
$q_1^{\mathrm{L,U}}$	$\frac{831}{166126}$	$\frac{146}{29187}$	$\frac{1}{11919}$	$\frac{1}{11921}$	$\frac{1}{6214}$	$\frac{13}{80783}$	$\frac{1}{7739}$	$\frac{4}{30957}$	$\frac{1}{24653}$	$\frac{1}{24659}$
$q_2^{\mathrm{L,U}}$	$\frac{295}{49966}$	$\frac{497}{84180}$	$\frac{1}{16432}$	$\frac{2}{32863}$	$\frac{1}{11953}$	$\frac{8}{95623}$	$\frac{1}{13225}$	$\frac{1}{13222}$	$\frac{1}{22667}$	$\frac{1}{22662}$
$q_3^{\mathrm{L,U}}$	$\frac{167}{70086}$	$\frac{133}{55817}$	$\frac{1}{62094}$	$\frac{1}{62095}$	$\frac{1}{62094}$	$\frac{1}{62095}$	$\frac{1}{62094}$	$\frac{1}{62095}$	$\frac{1}{62094}$	$\frac{1}{62095}$

Table 2 Coefficients of the upper bound polynomials T^{U}, $\tilde{Q}^{\mathrm{L,U}}$, and $\tilde{P}^{\mathrm{L,U}}$

	^{1}S		^{3}S		^{1}P		^{3}P		^{3}P$^{\mathrm{o}}$	
	T^{U}		T^{U}		T^{U}		T^{U}		T^{U}	
t_0^{U}	$\frac{8753}{9098}$		$\frac{249}{739}$		$\frac{3377}{7735}$		$\frac{15306}{39277}$		$\frac{8303}{26674}$	
t_1^{U}	$\frac{157}{72}$		$\frac{493}{288}$		$\frac{493}{288}$		$\frac{493}{288}$		$\frac{169}{288}$	
	$\tilde{P}^{\mathrm{L}}$	$\tilde{P}^{\mathrm{U}}$	$\tilde{P}^{\mathrm{L}}$	$\tilde{P}^{\mathrm{U}}$	$\tilde{P}^{\mathrm{L}}$	$\tilde{P}^{\mathrm{U}}$	$\tilde{P}^{\mathrm{L}}$	$\tilde{P}^{\mathrm{U}}$	$\tilde{P}^{\mathrm{L}}$	$\tilde{P}^{\mathrm{U}}$
$\tilde{p}_0^{\mathrm{L,U}}$	$\frac{333}{10288}$	$\frac{1684}{52027}$	$\frac{28}{11505}$	$\frac{46}{18901}$	$\frac{59}{10134}$	$\frac{181}{31089}$	$\frac{34}{9007}$	$\frac{113}{29935}$	$\frac{33}{22793}$	$\frac{13}{8979}$
$\tilde{p}_1^{\mathrm{L,U}}$	$\frac{95}{2208}$	$\frac{1078}{25055}$	$\frac{63}{28477}$	$\frac{56}{25313}$	$\frac{9}{2717}$	$\frac{64}{19321}$	$\frac{238}{85389}$	$\frac{9}{3229}$	$\frac{25}{13956}$	$\frac{57}{31820}$
$\tilde{p}_2^{\mathrm{L,U}}$	$\frac{889}{46656}$	$\frac{889}{46656}$	$\frac{5}{6337}$	$\frac{38}{48161}$	$\frac{5}{6337}$	$\frac{38}{48161}$	$\frac{5}{6337}$	$\frac{38}{48161}$	$\frac{5}{6337}$	$\frac{38}{48161}$
	$\tilde{Q}^{\mathrm{L}}$	$\tilde{Q}^{\mathrm{U}}$	$\tilde{Q}^{\mathrm{L}}$	$\tilde{Q}^{\mathrm{U}}$	$\tilde{Q}^{\mathrm{L}}$	$\tilde{Q}^{\mathrm{U}}$	$\tilde{Q}^{\mathrm{L}}$	$\tilde{Q}^{\mathrm{U}}$	$\tilde{Q}^{\mathrm{L}}$	$\tilde{Q}^{\mathrm{U}}$
$\tilde{q}_0^{\mathrm{L,U}}$	$\frac{25}{5308}$	$\frac{47}{9979}$	$\frac{1}{11647}$	$\frac{11}{128116}$	$\frac{3}{8104}$	$\frac{10}{27013}$	$\frac{1}{5732}$	$\frac{7}{40119}$	$\frac{1}{39011}$	$\frac{1}{38996}$
$\tilde{q}_1^{\mathrm{L,U}}$	$\frac{113}{12133}$	$\frac{78}{8375}$	$\frac{1}{9468}$	$\frac{8}{75749}$	$\frac{24}{86399}$	$\frac{1}{3600}$	$\frac{1}{5684}$	$\frac{13}{73893}$	$\frac{1}{19395}$	$\frac{1}{19396}$
$\tilde{q}_2^{\mathrm{L,U}}$	$\frac{53}{6856}$	$\frac{67}{8667}$	$\frac{2}{30477}$	$\frac{1}{15238}$	$\frac{2}{19625}$	$\frac{1}{9812}$	$\frac{3}{35497}$	$\frac{1}{11832}$	$\frac{1}{19951}$	$\frac{1}{19947}$
$\tilde{q}_3^{\mathrm{L,U}}$	$\frac{34}{14269}$	$\frac{31}{13010}$	$\frac{1}{62094}$	$\frac{1}{62095}$	$\frac{1}{62094}$	$\frac{1}{62095}$	$\frac{1}{62094}$	$\frac{1}{62095}$	$\frac{1}{62094}$	$\frac{1}{62095}$

Proof The bounds (10) follow in a straightforward way from the estimates (8) by taking into account the nonnegativity or nonpositivity of $Q^{\mathrm{L,U}}(Z)$ and $\tilde{Q}^{\mathrm{L,U}}(Z)$ on the respective Z domains and the fact that the terms $\cos F(Z)$, $\cos F(Z) - \sqrt{3}\sin F(Z)$ in (4) have a definite sign for all $Z \geq 0$. □

Table 3 Estimates of the real roots $Z_0^{\mathrm{L,U}}$, $\tilde{Z}_0^{\mathrm{L,U}}$ of $Q^{\mathrm{L,U}}$, $\tilde{Q}^{\mathrm{L,U}}$ and of the crossings Z_i^{cr} between E_i^{LB} and E_4^{B}, $i = 1, 2, 3$, the fraction given first being a lower bound, the second one an upper bound

	^{1}S		^{3}S		^{1}P		^{3}P		^{3}P$_{\mathrm{un}}$	
Z_0^{L}	$\frac{4231}{4067}$	$\frac{3973}{3819}$	$\frac{1031}{625}$	$\frac{8667}{5254}$	$\frac{8287}{3982}$	$\frac{1642}{789}$	$\frac{1379}{709}$	$\frac{4526}{2327}$	$\frac{1457}{1072}$	$\frac{6021}{4430}$
Z_0^{U}	$\frac{3173}{3050}$	$\frac{6217}{5976}$	$\frac{10702}{6477}$	$\frac{9091}{5502}$	$\frac{2927}{1406}$	$\frac{5294}{2543}$	$\frac{2154}{1105}$	$\frac{9193}{4716}$	$\frac{8753}{6379}$	$\frac{483}{352}$
$\tilde{Z}_0^{\mathrm{L}}$	$\frac{19042}{12371}$	$\frac{2569}{1669}$	$\frac{1502}{685}$	$\frac{6429}{2932}$	$\frac{13663}{4302}$	$\frac{740}{233}$	$\frac{4580}{1709}$	$\frac{10709}{3996}$	$\frac{5524}{2995}$	$\frac{1138}{617}$
$\tilde{Z}_0^{\mathrm{U}}$	$\frac{14988}{9737}$	$\frac{6485}{4213}$	$\frac{261}{119}$	$\frac{5549}{2530}$	$\frac{9641}{3035}$	$\frac{8256}{2599}$	$\frac{6232}{2325}$	$\frac{1493}{557}$	$\frac{1211}{656}$	$\frac{7290}{3949}$
Z_1^{cr}	$\frac{2183}{2319}$	$\frac{8106}{8611}$	$\frac{4501}{3196}$	$\frac{12420}{8819}$	$\frac{3574}{2181}$	$\frac{957}{584}$	$\frac{14265}{8912}$	$\frac{3443}{2151}$	$\frac{5487}{4295}$	$\frac{290}{227}$
Z_2^{cr}	$\frac{205}{118}$	$\frac{5502}{3167}$	$\frac{3764}{1747}$	$\frac{7291}{3384}$	$\frac{6528}{2693}$	$\frac{1229}{507}$	$\frac{7519}{3198}$	$\frac{2946}{1253}$	$\frac{2535}{1219}$	$\frac{3319}{1596}$
Z_3^{cr}	$\frac{3540}{1049}$	$\frac{24888}{7375}$	$\frac{13165}{3138}$	$\frac{14067}{3353}$	$\frac{6143}{1354}$	$\frac{3870}{853}$	$\frac{31155}{6994}$	$\frac{31400}{7049}$	$\frac{3557}{858}$	$\frac{4183}{1009}$

3 Applications

To illustrate the application of the bounds established in the preceding section, below we study an example within the theory of atomic Schrödinger operators. In 1983, Simon [15] formulated a conjecture about the monotonicity of ionization energies. Although this conjecture appears highly plausible by heuristic arguments and is in accordance with all experimental data, until today only very little progress has been achieved [3] towards its general solution. If $E_i(Z, N)$ denotes the ith energy level of an atomic Hamiltonian $H(Z, N)$ (constructed in analogy to (1)) and $E_\infty(Z, N) = \inf \sigma_{\mathrm{ess}}(H(Z, N))$ the threshold of the continuous spectrum of $H(Z, N)$, then the monotonicity conjecture claims that

$$\mathrm{IP}(Z, N) \geq \mathrm{IP}(Z, N + 1) \tag{12}$$

for all $Z > 0$ and $N = 1, 2, \ldots$. Here, the ionization potential IP is given by $\mathrm{IP}(Z, N) = E_\infty(Z, N) - E_1(Z, N)$, and the situation is displayed schematically in Figure 1. In the simplest case, $N = 1$, the relation (12) is equivalent to $Z^2 + E_1(Z, 2) \geq 0$. Actually, to prove the stronger inequality

$$Z^2 + E_1^{\mathrm{LB}}(Z, 2) > 0, \tag{13}$$

we merely need to resort to (the parabolic version of) lower bounds from one-dimensional projections [8], viz., $E_1^{\mathrm{LB}}(Z, 2) = \min\{-(Z - Z_L)^2, E_2^{\mathrm{B}}(Z)\}$ with $Z_L = 128(1 - \sqrt{5/8})/105$ for which (13) can be verified easily.

One may extend Simon's conjecture by regarding excitation energies $\Delta E_j(Z, N) = E_j(Z, N) - E_1(Z, N)$ not only to the ioniziation threshold, but also to less excited energy levels. The monotonicity

$$\Delta E_j(Z, N) \geq \Delta E_j(Z, N + 1) \tag{14}$$

can be physically explained as a manifestation of the screening effect in atoms: N electrons shield an additional electron more strongly against the attractive nuclear

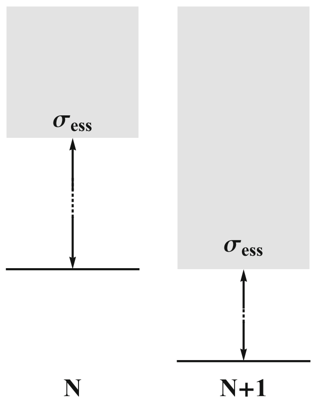

Fig. 1 Schematic comparison of the spectral properties of relevance for ionization energies of atoms with N and $N+1$ electrons

charge than $N-1$ electrons do, therefore causing a reduced level spacing. For $N=1$ and the two-electron states considered in Sect. 2, the relation (14) means

$$\begin{aligned} \Delta E\Big(Z; 2^1\mathrm{S}, 2^3\mathrm{S}, 2^1\mathrm{P}, 2^3\mathrm{P}\Big) &\le -\frac{Z^2}{8}+\frac{Z^2}{2}=\frac{3Z^2}{8} \\ \Delta E\ \Big(Z; 3^1\mathrm{S}, 3^3\mathrm{S}, 3^1\mathrm{P}, 3^3\mathrm{P}\Big) &\le -\frac{Z^2}{8}+\frac{Z^2}{2}=\frac{3Z^2}{8} \\ \Delta E\Big(Z; 4^3\mathrm{S}, 4^1\mathrm{P}, 4^3\mathrm{P}\Big) &\le -\frac{Z^2}{8}+\frac{Z^2}{2}=\frac{3Z^2}{8}. \end{aligned} \tag{15}$$

In (15) we invoked the standard spectroscopic notation for the two-electron states with $\Delta E(Z; 2^1\mathrm{S}) = E(Z; 2^1\mathrm{S}) - E(Z; 1^1\mathrm{S})$ and analogously for the other states.

While a similar analysis can also be performed for the first two inequalities in (15), in the sequel we focus onto the last one because for this inequality the application of bounds from three-dimensional projections becomes essential. Graphically, a verification could proceed by plotting the elementary functions occurring in (10) as depicted in Fig. 2. A rigorous statement reads as follows.

Theorem 3.1 *For* $35/158 \le Z \le 432738/113 \approx 3829.5$ *the inequality holds*

$$\max\left\{E_3^{\mathrm{UB}}(Z;{}^3\mathrm{S}), E_3^{\mathrm{UB}}(Z;{}^1\mathrm{P}), E_3^{\mathrm{UB}}(Z;{}^3\mathrm{P})\right\} - E_1^{\mathrm{LB}}(Z;{}^1\mathrm{S}) \le \frac{15Z^2}{32} \tag{16}$$

and implies the validity of the last estimate in (15) *for* $0 < Z < 432738/113$.

Proof For Z below ≈ 4, the maximum in (16) is attained by the upper bound for the ${}^1\mathrm{P}$ state. Thus we set

$$F_1(Z) = \frac{15Z^2}{32} - \left(E_3^{\mathrm{UB}}(Z;{}^1\mathrm{P}) - E_1^{\mathrm{LB}}(Z;{}^1\mathrm{S})\right) \tag{17}$$

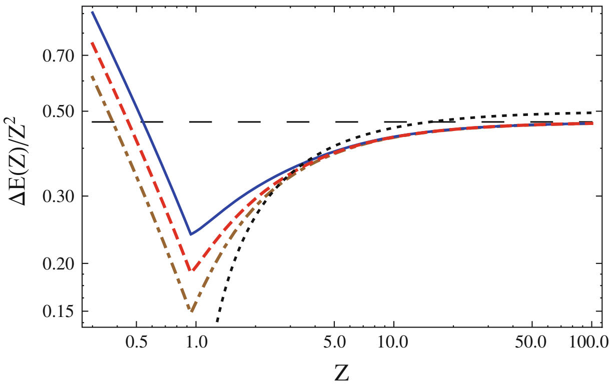

Fig. 2 Energy difference $(E_3^{\mathrm{UB}}(Z;{}^1\mathrm{P}) - E_1^{\mathrm{LB}}(Z;{}^1\mathrm{S}))/Z^2$ (*solid line*), $(E_3^{\mathrm{UB}}(Z;{}^3\mathrm{P}) - E_1^{\mathrm{LB}}(Z;{}^1\mathrm{S}))/Z^2$ (*dashed line*), $(E_3^{\mathrm{UB}}(Z;{}^3\mathrm{S}) - E_1^{\mathrm{LB}}(Z;{}^1\mathrm{S}))/Z^2$ (*dashed dotted line*), $(E_\infty(Z) - E_1^{\mathrm{LB}}(Z;{}^1\mathrm{S}))/Z^2$ (*dotted line*) and the value 15/32 indicated by a *long-dashed line*

where for $Z \le Z_{\mathrm{cr}}$ we have to employ $E_1^{\mathrm{LB}}(Z;{}^1\mathrm{S}) = E_4^{\mathrm{B}}(Z)$. Using that $|\cos x| \le 1$, we get

$$F_1(Z) \ge \frac{1357Z^2}{864} - \frac{3377Z}{23205} - 2Z\sqrt{\frac{38Z^2}{48161} - \frac{64Z}{19321} + \frac{181}{31089}}, \tag{18}$$

in which the last term obeys

$$\sqrt{c_2Z^2 + c_1Z + c_0} \le \sqrt{c_2}\sqrt{(Z + c1/(2c_2))^2} + \sqrt{c_0 - c_1^2/(4c_2)} \tag{19}$$

so that, after also estimating terms with proliferating digits, we arrive at

$$F_1(Z) \ge \frac{1357Z^2}{864} - \frac{3377Z}{23205} - 2Z\left(\sqrt{\frac{38Z^2}{48161}}\left(\frac{233}{111} - Z\right) + \sqrt{\frac{1}{426}}\right) \tag{20}$$

which is a polynomial of second degree in Z with roots $Z_1 = 0$ and $Z_2 < 35/158$, and which becomes positive for $Z > Z_2$. If $Z_{\mathrm{cr}} \le Z \le 128/105$, we can use $E_1^{\mathrm{LB}}(Z;{}^1\mathrm{S}) = E_2^{\mathrm{B}}(Z)$ as lower bound in (17). This only changes the first term in (18) into $719Z^2/432$, and in the same way as before leads to a polynomial with roots $Z_1 = 0$, $Z_2 < 35/128$ and positivity for $Z > Z_2$. If $128/105 \le Z \le 233/111$, we take the lower bound $E_1^{\mathrm{LB}}(Z;{}^1\mathrm{S}) = -Z^2 + 16Z/35)$ from a one-dimensional projection [8]. Then the first two terms on the right hand side of (18) become $17Z^2/432 + 1033Z/3315$, producing a polynomial having roots $Z_1 = 0$ and $Z_2 < 126/229$ and again being positive for $Z > Z_2$. If $Z > 233/111$, we still can use the same E_1^{LB}, but have to revert the sign of the term $233/111 - Z$. The ensuing polynomial is positive for $0 < Z < Z_2$ with $737/156 < Z_2 < 600/127$, thus covering the remaining Z

range where $E_3^{\mathrm{UB}}(Z;{}^1\mathrm{P})$ provides the maximum in (16). For larger Z, the maxium is attained by $E_3^{\mathrm{UB}}(Z;{}^3\mathrm{P})\}$ and we define

$$F_2(Z) = \frac{15Z^2}{32} - \left(E_3^{\mathrm{UB}}(Z;{}^3\mathrm{P}) - E_1^{\mathrm{LB}}(Z;{}^1\mathrm{S})\right) \tag{21}$$

with $E_1^{\mathrm{LB}}(Z;{}^1\mathrm{S})$ from the one-dimensional projection. Then, with $g(Z) = \tilde{Q}^{\mathrm{U}}(Z)/(\tilde{P}(Z))^{3/2}$,

$$\begin{aligned}
F_2(Z) &= \frac{17Z^2}{432} + \frac{64266Z}{196385} - 2Z\sqrt{\frac{38Z^2}{48161} - \frac{9Z}{3229} + \frac{113}{29935}}\cos\frac{1}{3}\arccos g(Z) \\
&\geq \frac{17Z^2}{432} + \frac{64266Z}{196385} - 2Z\left(\sqrt{\frac{38Z^2}{48161}} + \sqrt{\frac{113}{29935}}\right)\cos\frac{1}{3}\arccos g(Z) \\
&\geq \frac{17Z^2}{432} + \frac{64266Z}{196385} - 2Z\left(\sqrt{\frac{38Z^2}{48161}} + \sqrt{\frac{113}{29935}}\right)
\end{aligned} \tag{22}$$

yielding a polynomial that is positive between its roots $Z_1 = 0$ and $< Z_2 \approx 12.45$. On the other hand, for $Z \geq 12$ we will show that

$$g_0 = -\frac{5913}{8174} > g(12) \geq g(Z) \geq -1 \tag{23}$$

so that by employing $\cos\frac{1}{3}\arccos g(Z) \leq \cos\frac{1}{3}\arccos g_0 < 1982/2825$ in (22) we get a positive polynomial for $0 < Z < Z_2$ where the second root obeys $Z_2 > 432738/113$. It remains to show (23). To infer $g(Z) \geq -1$, since $\tilde{Q}^{\mathrm{U}}(Z) < 0$ it is sufficient to prove $0 < (\tilde{P}^{\mathrm{U}}(Z))^3 - (\tilde{Q}^{\mathrm{U}}(Z))^2 = \sum_{k=0}^{6} a_k Z^k$. By analyzing $\partial(\sum_{k=0}^{5} a_{k+1}Z^k)/\partial Z$, the monotonic decrease of $\sum_{k=0}^{5} a_{k+1}Z^k$ is easily verified, and, computing $\sum_{k=0}^{5} a_{k+1}4^k > 0$, we get $0 < Z\sum_{k=0}^{5} a_{k+1}Z^k < \sum_{k=0}^{6} a_k Z^k$ for $Z \geq 4$. Next, to establish $g_0 > g(Z)$, it suffices to demonstrate $G(Z) = \sum_{k=0}^{6} b_k Z^k = g_0^2(\tilde{P}^{\mathrm{U}}(Z))^3 - (\tilde{Q}^{\mathrm{U}}(Z))^2 < 0$. But, employing that $G^{(n)}(12) < 0$ for all derivatives $n = 0, 1, \ldots, 6$, and, starting with $G^{(6)}(Z) = \mathrm{const} < 0$, the monotonic decrease of $G^{(5)}$ results, and, continuing iteratively until $n = 0$, the monotonic decrease of all $G^{(k)}$ can be deduced. Finally, to infer the last inequality in (15) for the not yet considered $Z \in (0, 35/158]$, it sufficies to observe that for $Z \leq 1$ the minimum in the upper bound (10) is attained by $E_\infty(Z)$ and that $E_\infty(Z) - E_4^{\mathrm{B}}(Z) = Z^2/32$. □

By Theorem 3.1 all elements found in nature are settled; nonetheless, we expect the monotonicity properties to be valid for all $Z > 0$. Since however for $Z \to \infty$ the left hand sides of (15) will approach and get arbitrarily close to their respective right hand sides, to separate them by upper and lower bounds requires bounds that converge sufficiently rapidly to the exact energies upon $Z \to \infty$. Unfortunately, this

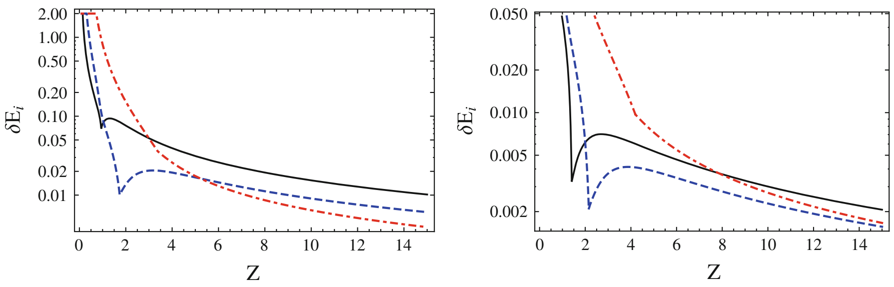

Fig. 3 Relative differences δE_i between the upper and lower bounds for $i = 1$ (*solid line*), $i = 2$ (*dashed line*), $i = 3$ (*dashed-dotted line*) and ^{1}S states (*left panel*) and ^{3}S states (*right panel*)

is not the case for the bounds (10); inserting their asymptotics, it turns out that (16) will definitely be violated if $Z \geq 2 \times 10^6$.

4 Discussion and conclusions

As we pointed out in the introduction, our emphasis lies not on numerical results but on explicit bounds amenable to analytic calculations. Thus, the bounds derived in Sect. 2 are not supposed to compete with numerical high precision computations. To assess the quantitative behaviour of the bounds (10), in Fig. 3 we display the relative differences $\delta E_i = (E_i^{\mathrm{UB}} - E_i^{\mathrm{LB}})/(|E_i^{\mathrm{UB}}/2| + |E_i^{\mathrm{LB}}|/2)$ between the upper and lower bounds for the ^{1}S and ^{3}S states. For the ground state 1^1S and Z associated to neutral or positively charged systems, δE_1 remains below $\approx$7%, but rises to almost 10% for Z around the negatively charged ion H^-. Furthermore, apparently the energies of the neutral or positively charged excited state 2^1S are much better approximated by the bounds than the ground state energies, so that $\delta E_2(Z) < \delta E_1(Z)$ on that Z range. As expected, due to the ever smaller relative contribution of electronic correlation to the total energy for growing Z, all curves δE_i decrease for large enough Z. Since the correlation in ^{3}S states also is expected to be weaker than in ^{1}S states, for neutral and positively charged systems the relative difference δE_i for the lowest two triplet states is significantly smaller than for the corresponding singlet states, viz., $\delta E_i(Z) < 1\%$, $i = 1, 2$. A behaviour very similar to the S states can be observed for the P states, hence we abstain from including analogous plots. Instead we compare bounds from one-, two-, and three-dimensional projections in Fig. 4.

Obviously, whereas δE_1 gets distinctly reduced when using two-dimensional rather than one-dimensional projections in (3), merely a minor reduction is achieved when passing from two- to three-dimensional projections. Actually, in the latter case the reduction is larger for the first excited states, though a more remarkable advantage of the three-dimensional projections—besides providing bounds for an additional (i.e., the second excited) state—is the shift of the values Z_i^{cr} of the crossings of the lower bound curves with the base levels to smaller numbers, thus enlarging the Z regions where nontrivial lower bounds are available.

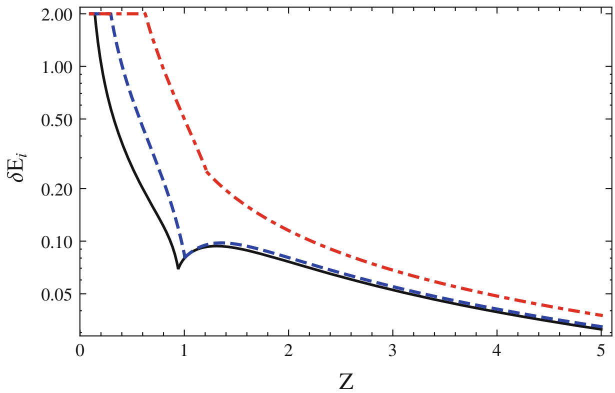

Fig. 4 Relative differences δE_1 between the upper and lower bounds derived from one-dimensional (*dashed-dotted line*), two-dimensional (*dashed line*), and three-dimensional (*solid line*) projections for the ground state 1^1S

Quantitatively, (10) yields the rigorous estimates

$$
\begin{aligned}
&-\frac{361}{149}-\sqrt{\frac{305}{733}}\sin\left(\frac{\pi}{6}+\frac{1}{3}\arccos-\sqrt{\frac{711}{800}}\right)<E_1(2;\,1^1\mathrm{S}),\\
&E_1(2;\,1^1\mathrm{S})<-\frac{213}{94}-\frac{1}{27}\sqrt{\frac{1523172}{5795}}\sin\left(\frac{\pi}{6}+\frac{1}{3}\arccos-\frac{38208}{775}\sqrt{\frac{1}{6571}}\right),\\
&-\frac{3733}{7704}-\frac{1}{108}\sqrt{\frac{109149}{1346}}\sin\left(\frac{\pi}{6}+\frac{1}{3}\arccos\frac{1918}{965}\sqrt{\frac{11}{892}}\right)<E_1(1;\,1^1\mathrm{S}),\\
&E_1(1;\,1^1\mathrm{S})<-\frac{132}{325}-\frac{1}{108}\sqrt{\frac{396854}{1013}}\sin\left(\frac{\pi}{6}+\frac{1}{3}\arccos-\frac{23641}{1235}\sqrt{\frac{4}{1567}}\right),
\end{aligned}
\tag{24}
$$

i.e., $-3.0637\ldots < -2.9037\ldots < -2.8387\ldots$ and $-0.5535\ldots < -0.5277\ldots < -0.5110\ldots$ for the ground state energies of the He atom and H^- ion, respectively.

In Sect. 3 we employed the bounds (10) for establishing monotonicity properties of the excitation energies with respect to the number N of electrons. Monotonicity of excitation energies also holds with respect to Z [16] and the bounds can equally be utilized to improve and extend the results for this monotonicity. Further specific prospects for the application of (10) are the ionization energy conjecture mentioned in Sect. 3 and the analysis of level ordering and stability of matter problems [17].

Note added in proof. As a further application of the bounds established in Theorem 2.1, the stability of the atomic anion He^- with Bosonic electrons is demonstrated in [18].

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