Improved calculation of the electron affinity of He $1s\,2s\ ^3S$

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Large-scale optimization of nonlinear parameters and tighter error-bound estimates yield an accurate value, $E_{\rm nr}=-2.178\,077\,6(12)$ a.u. (^{4}He) for the nonrelativistic energy of He$^-$ $1s\,2s\,2p\ ^4P^o$, in agreement with a previous result of $-2.178\,074\,0(100)$. Using Chung's recent calculation of relativistic and mass-polarization effects, an electron affinity $A=77.51\pm0.04$ meV is obtained. The calculation and significance of error bars in electronic structure calculations is discussed.

Five years ago,[1] we carried out configuration-interaction (CI) calculations on He$^-$ $1s\,2s\,2p\ ^4P^o$, and estimated the nonrelativistic part of the electron affinity of He $1s2s\ ^3S$ as $A_{\rm nr}=77.4\pm0.3$ meV. We also argued that relativistic, radiative, and mass-polarization effects, $A_{\rm rrmp}$, should contribute no more than ±0.2 meV, so that the total electron affinity, $A=A_{\rm nr}+A_{\rm rrmp}$, was finally reported as $A=77.4\pm0.5$ meV.

Recently, in an effort to reduce the uncertainty caused by $A_{\rm rrmp}$, Chung[2] studied relativistic and mass-polarization effects in He$^-$ $1s2s2p\ ^4P^o_{5/2}$, and found them to be equal to -115.0 μhartree. The fine-structure levels in He$^-$ are inverted, so that $J=\frac{5}{2}$, the lowest state, defines the reference negative ion state in the electron affinity calculation. By combining Chung's result with a correspondingly accurate estimate for He $1s2s\ ^3S_1$ of -114.4 μhartree,[3] one gets $A_{\rm rrmp}=0.016\pm0.010$ meV, assuming a radiative correction of ±0.010 meV, which is likely to be too large. Therefore, one may write the electron affinity as

$$A=A_{\rm nr}+0.016\pm0.010\ \text{meV}\ , \tag{1}$$

which means that the major source of uncertainty in A now lies in the value of $A_{\rm nr}$. The purpose of this work is to reduce this uncertainty by one order of magnitude, from 0.30 down to 0.03 meV, which requires the calculation of an eigenvalue of Schrödinger's nonrelativistic equation for a three-electron system with an unprecedented uncertainty of 10^{-6} a.u. ($=1$ μhartree).

Besides an intrinsic interest[1] in obtaining a more accurate value of the electron affinity of helium, we were motivated by a persistent skepticism within the physics community concerning the possibility of estimating meaningful error bounds in electronic structure calculations, to the extent that most calculations in this field do not include even the most rudimentary type of error analysis. One powerful reason to ignore this fundamental problem is that known rigorous methods[4] perform poorly, providing error bounds which are too large for practical purposes.[5]

In two-electron calculations with perimetric coordinates,[6] the frontier of accurate many-electron calculations, convergence patterns for expectation values show up explicitly, and the accuracy achieved is so impressive that the empirical nature of the extrapolations involved is usually forgotten. In many-electron orbital calculations, on the other hand, the analysis of invariant quantities, such as energy contributions[7,8] associated with natural orbitals,[9] leads to less accurate energies, and only after going through very laborious procedures.[10] A remarkable example is the energy obtained for the He ground state,[8] $E_{\rm extr}=-2.903\,724\,25$ a.u. (to be compared with $E_{\rm exact}=-2.903\,724\,38$),[11] after extrapolations from a set of variational CI wave functions, none of which gives an energy lower than $-2.903\,300$. These extrapolations are based on empirical observations of patterns of convergence of quantities which, in the limit of very large basis sets, acquire well-defined values.

One important practical result from convergence studies in CI calculations is the approximate additivity[10] of truncation energy errors associated with invariant portions of the wave function, such as pair-electron functions. For example, if $\Delta E_{\rm inn}$, $\Delta E_{\rm int}$, and $\Delta E_{\rm out}$ are the truncation energy errors associated with the inner-shell excitations, inter-shell and outer-shell excitations, respectively, the total truncation energy error is well approximated by the sum of these three quantities.

The existence of patterns of convergence for energy contributions suggests more crude sensitivity tests, similar in spirit to those performed in assessing the approximate simulation of any process. Instead of recurring to asymptotically invariant quantities, which are difficult to evaluate, one can study the successive addition of energy optimized functions to each portion of the wave function, separately. Usually, each new step requires the effective reoptimization of all the previously determined basis functions. The corresponding energy decrements are assumed to be approximate invariants within a particular class of basis sets, viz., Slater-type orbitals (STO's). If saturation is reached within a reasonably prescribed threshold of energy decrements, one may have arrived at true convergence for a given class of symmetry orbitals, say,

TABLE I. Energy optimized STO parameters used in the final wave function. The total STO truncation energy error $\Delta E_{\rm STO}$ is equal to -5.8 ± 1.1 μhartree.

Wave function	STO's
$\Psi_{\rm outer}$	$1s=2.00$; $2s=1.438$; $2s=0.945$; $2s=0.629$; $2s=0.393$; $2s=0.215$
	$2p=1.89$; $2p=0.880$; $2p=0.518$; $2p=0.269$; $2p=0.128$; $4p=1.090$
	$3d=0.97$; $3d=0.320$; $4d=1.03$; $4d=0.377$; $4f=0.60$; $5f=0.69$
	$6f=1.12$; $5g=0.93$; $6g=0.93$; $6h=1.12$
$\Psi_{\rm inter}$	same STO's as for $\Psi_{\rm outer}$ plus
	$2s=2.30$; $3s=2.40$; $4p=1.68$; $5p=3.04$
	(d-STO's reoptimized in $\Psi_{\rm core}$ below),
	$4f=1.77$; $5f=1.88$; $5g=2.22$; $6g=2.20$
$\Psi_{\rm core}$	same STO's as for $\Psi_{\rm inter}$ plus
	$4s=2.70$; $5s=3.85$; $6p=3.00$; $7p=4.10$
	$3d=1.44$; $4d=2.16$; $5d=1.67$; $6d=1.84$; $4f=3.00$

d-type orbitals, and for a given invariant portion of the wave function, say, the outer-shell excitations. In order to verify whether the convergence is spurious or not, there is no other known recipe than to try a variety of basis sets and optimization strategies. In this way it has been possible to calculate transition wavelengths to spectroscopic accuracy,[12] with significant consequences in the elucidation of atomic spectra.

After the STO truncation energy error $\Delta E_{\rm STO}$ is calculated, the nonrelativistic energy $E_{\rm nr}$ is written as

$$E_{\rm nr}=E_u+\Delta E_{\rm STO}+\Delta E_{\rm CI}\ , \tag{2}$$

where E_u is a rigorous variational upper bound, and $\Delta E_{\rm CI}$ denotes the truncation energy error due to any simplification to the full CI effected in the evaluation of E_u.

The strategy outlined above will now be made explicit for the construction of an energy optimized STO set for He$^-$ $1s2s2p\ ^4P^o$. We start by approximating a $1s$ orbital by a single STO with orbital exponent $\alpha=2$. We also define an outer-shell expansion $\Psi_{\rm outer}$ as a complete CI keeping the $1s$ orbital fixed

$$\Psi_{\rm outer}=\Lambda\left[1s\sum_{a,b}\phi_a\phi_b o_{ab}\right]\ , \tag{3}$$

where the ϕ_a's are symmetry-adapted spin orbitals, Λ is the product of the antisymmetrizer with a spin and orbital angular momentum projection operator, and the o_{ab}'s are expansion coefficients. After a careful energy optimization of STO parameters, which is carried out to within a few thousandths of one μhartree, we obtained a $6s6p4d3f2g1h$ STO basis given in the upper part of Table I. We tested many other possible combinations of STO's with other principal quantum numbers; for example, the STO $4p=1.09$ could have been a $3p$ or a $2p$ with a different orbital exponent and a net energy penalty of 0.022 μhartree. A still larger basis of $8s8p6d4f3g2h1i$ energy optimized STO's (not shown) was used to detect a definite pattern of energy convergence for each harmonic type. In this way we found an extrapolated energy which, when combined with the outer-shell CI energy obtained with our final STO basis, yielded an outer-shell STO truncation energy error $\Delta E_{\rm STO}=-1.2\pm0.4$ μhartree, as reported in Table II.

TABLE II. STO truncation energy errors, $\Delta E_{\rm STO}$, in μhartree, for different invariant portions of the He$^-$ $1s2s2p\ ^4P^o$ wave function.

l	$2s$, $2p$, and $2s2p$ excitations	$1s$ and $1s2p$ excitations	$1s2s$ excitations
≤ 2	0.4 ± 0.2	0.9 ± 0.4	
≥ 3	0.8 ± 0.2	0.4 ± 0.2	
total	1.2 ± 0.4	1.3 ± 0.6	3.3 ± 0.1

We now chose the orbitals $2s$ and $2p$ as the major natural orbitals of $\Psi_{\rm outer}$ and proceeded to define $\Psi_{\rm inter}$ as

$$\Psi_{\rm inter}=\Lambda\left[2s\sum_{a,b}\phi_a\phi_b i_{ab}\right]\ , \tag{4}$$

excluding $2p$ single excitations. A similar energy optimization yielded an additional $2s2p2d2f2g$ STO basis, given in the middle part of Table I, except for the d orbitals, which were later modified. Analogously as before, we get an inter-shell STO truncation energy error $\Delta E_{\rm STO}=-1.3\pm0.6$ μhartree, also shown in Table II.

Finally, we considered $\Psi_{\rm core}$,

$$\Psi_{\rm core}=\Lambda\left[2p\sum_{a,b}\phi_a\phi_b c_{ab}\right]\ , \tag{5}$$

expressing electron correlations in the $1s2s$ core. Here, the energy optimization of STO parameters, given in the lower part of Table I, was performed directly upon He $1s2s\ ^3S$. As we verified that each new STO introduced into this wave function produced energy decrements equal to those in the three-electron wave function $\Psi_{\rm core}$, we can safely approximate $\Delta E_{\rm STO}$(core) as

$$\Delta E_{\rm STO}({\rm core})=E_{\rm exact}({\rm He}\ ^3S)-E_{\rm final\ basis}({\rm He}\ ^3S)$$
$$=-3.3\pm0.1\ \mu{\rm hartree}\ , \tag{6}$$

where $E_{\rm exact}({\rm He}\ ^3S)=-2.175\,2293$ a.u.(^{4}He).[3] After carrying out the full CI, we also verified that triple excitations contribute to $\Delta E_{\rm STO}$ with less than 0.1 μhartree. Adding up the STO truncation energy errors of Table II we get

$$\Delta E_{\rm STO}=-5.8\pm1.1\ \mu{\rm hartree}\ . \tag{7}$$

TABLE III. Electronic energy $E_{\rm nr}$ of $\rm He^-$ $1s2s2p\ ^4P^o$, in a.u., and electron affinity of He $1s2s\ ^3S$. 1 a.u. (^{4}He)$=219\,444\,53$ $\rm cm^{-1}=27.207\,91(10)$ eV.

	Energy correction	Total energy
E_u, 1000-term CI		$-2.178\,0713$
Truncation error, $\Delta E_{\rm CI}$	$-0.000\,000\,5(1)$	
Truncation error, $\Delta E_{\rm STO}$	$-0.000\,005\,8(11)$	
$E_{\rm nr}$		$-2.178\,077\,6(12)$
$A_{\rm nr}=E_{\rm nr}-E_{\rm nr}({\rm He}\ 1s2s\ ^3S)^{\rm a}$	$-0.002\,848\,3(12)=77.50\pm0.03$ meV	
A, Eq. (1)	77.51 ± 0.04 meV	

[a]Obtained from Ref. 3; $E_{\rm nr}$ (He $1s2s\ ^3S$)$=-2.175\,2293$ a.u. (^{4}He).

Notice that except for the negligible $\Delta E_{\rm STO}$(triples), we arrived at (7) before we had any idea about the value of E_u in Eq. (2). Preliminary calculations of E_u with smaller STO basis would have served no purpose.

We now have to evaluate the variational energy upper bound E_u, which for a $10s10p8d6f4g1h$ orbital basis corresponds to a 6337-term CI. State of the art computer programs, such as used in molecular calculations, should easily handle atomic CI expansions of this size, and even much larger ones.[13] Our older[10,14] but widely verified double precision (22 ciphers) codes, however, become increasingly inefficient for CI sizes much larger than 1500, execution times being roughly divided between the generation of the Hamiltonian matrix and the evaluation of one eigenvector and eigenvalue to within one thousandth of a μhartree, using Davidson's algorithm.[15] Therefore, we carried out several 1000-term CI calculations which consume about 15 minutes of a Burroughs 7800 computer.[16] Although CI truncations are guided by partial energy contributions for each configuration,[17] the total CI truncation energy error $\Delta E_{\rm CI}$ is estimated[10] as a sum of partial $\Delta E_{\rm CI}$'s each one of them being calculated as a difference between variational energies of extended and truncated CI expansions. In Table III we collect all pertinent information for the calculation of $E_{\rm nr}$ and A. For the latter we get

$$A=77.51\pm0.04\ \text{meV}\ , \tag{8}$$

in agreement with less accurate previous theoretical results.[1,2]

Reliance on (8) rests on two grounds that cannot be dissociated from one another: (i) the fact that $\rm He^-$ $1s2s2p\ ^4P^o$ is within the range of validity of Schrödinger's equation and its perturbative corrections,[3,18] and (ii) the assumed correctness of the numerical procedures employed and their implementations. Current criticism falls usually on the latter. For example, all procedures sensitive to human error should eventually be taken over by robust computer programs which earned their foolproof status through successful performance in a variety of applications, such as the computer codes used in this work. High universality of component program modules and adequate data validation are prioritary assets for any electronic structure package. Furthermore, there are matters of principle, like whether true or spurious convergence has been achieved at any particular stage of the calculation. We claim that this question has been answered within a given domain, viz., CI atomic structure calculations. Under the constraints of present computer costs, however, multiparameter energy optimizations still require the artful work of a highly motivated individual. In this connection, given a capable worker with adequate computational means, it should not be assumed that her (his) compromise with maximum possible accuracy must be a permanent one. In fact, atomic CI calculations have matured to the point where the *desired* energy accuracy, as needed by a particular application, elicits well-defined requirements (basis sets, size of CI expansion) further translating into specific hardware and software demands. It is at this stage that one decides whether the proposed calculation is worth the trouble, or if it is at all feasible for a fixed amount of resources. Certainly, the quantitative determination of physical quantities, either theoretically or experimentally, will always be error prone, as superbly illustrated by a plot[19] which shows how our knowledge of the fine-structure constant and its one-standard-deviation uncertainty varied over the years.

At present, other methods like Hylleraas r_{ij} expansions[20] or hyperspherical coordinate calculations[21] are orders of magnitude less accurate than CI. Further progress, if warranted, is more likely to be expected from CI studies of patterns of convergence with piecewise polynomial basis sets.[8]

Among recent experiments on $\rm He^-\ ^4P^o$,[22,23] there stands out a study[23] of its photodetechment spectrum which is consistent with previous theoretical results[24] for the positions of $\rm He^-$ $1s2s2p\ ^4P^o$ and $1s2p^2\ ^4P$, respectively. A direct experimental test on (8), however, is likely to remain a challenge for some time.

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