Relativistic Coupled Cluster Calculations with Variational Quantum Electrodynamics Resolve the Discrepancy between Experiment and Theory Concerning the Electron Affinity and Ionization Potential of Gold

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The first ionization potential (IP) and electron affinity (EA) of the gold atom have been determined to an unprecedented accuracy using relativistic coupled cluster calculations up to the pentuple excitation level including the Breit and QED contributions. We reach meV accuracy (with respect to the experimental values) by carefully accounting for all individual contributions beyond the standard relativistic coupled cluster approach. Thus, we are able to resolve the long-standing discrepancy between experimental and theoretical IP and EA of gold.

The quantum electrodynamic (QED) treatment of free elementary particles like the electron or the muon is now well established [1]. For example, the anomalous magnetic moment of the electron $g - 2$ can be determined precisely to ~11 significant digits using summations over more than 10 000 terms of the tenth order Feynman diagrams including lowest order hadronic and electroweak contributions [2–4]. Together with experiments from a one-electron quantum cyclotron, this determines the precise value of the fine structure constant α as a stringent test of the standard model [5].

The situation is very different for bound state QED, especially when the nuclear charge $Z\alpha$ becomes large (strong Coulomb fields) [6,7]. Karshenboim pointed out that current *ab initio* QED calculations cannot present any theoretical prediction to compare with the precise measurements [8,9]. However, for few-electron systems, remarkable progress has been made over the past two decades [10], predicting energy levels including the hyperfine and the QED effects of highly charged ions to meV accuracy, or for the special case of the hydrogen atom, even down to peV accuracy [11]. For example, Beiersdorfer *et al.* measured the $2P_{1/2} - 2S_{1/2}$ transition energy of the lithiumlike uranium isotope $^{238}U^{89+}$ to be 280.645(15) eV [12], in very good agreement with the QED results by Kozhedub *et al.* [280.71(10) eV] [13].

In contrast, the computational treatment of multielectron systems with an accuracy that rivals experiment remains a great challenge. Here, the bottleneck lies in both the electron correlation and the QED treatment, as these are not strictly additive [14,15]. Considerable progress has been made for simple one- or two-valence-electron systems, which have energetically low lying cores that are well separated from the valence shell [16–18]. The usual approach to multielectron systems is to apply QED model operators for the lowest orders bound-state Feynman diagrams, such as the multiple commutator approach by Labzowsky and Goidenko [19,20], the covariant evolution operator method of Lindgren and co-workers [21], Shabaev's two-time Green's function method [15] and approximation to the electron self-energy by using local and nonlocal operators [22], or the approach by Ginges and Flambaum separating the self-energy term into a magnetic form factor plus low- and high-frequency parts [23,24]. For the vacuum polarization, the Uehling potential with a finite nucleus plus higher order terms, such as the Wichmann-Kroll and the Källén-Sabry corrections, are commonly used [25,26].

Au has a $6s^1$ ground state configuration and may formally be considered a one-valence electron system. However, due to the strong relativistic $6s$ stabilization and the indirect $5d$ expansion [27] (including spin-orbit coupling), the $5d/6s$ energy gap becomes small with a $^2S_{1/2} - {}^2D_{5/2}$ separation of only 1.14 eV [28]. In fact, the resulting soft and polarizable $5d$ shell is responsible for the enhancement of relativistic effects within the group 11 and 12 elements of the periodic table [29]. Moreover, correlating the $5d$ shell and the lower lying ($5s5p$) shells now becomes essential for any accurate determination of the valence electron spectrum of gold. We note that this group 11 (and 12) enhancement of relativistic effects has also been observed in the rather large QED contributions to the

ionization potential (IP) and electron affinity (EA) of the gold atom [24].

State-of-the-art Fock-space coupled cluster calculations [30] adding QED included perturbatively [24] at the Dirac–Hartree–Fock level reveals a rather large discrepancy of 0.16 and 0.05 eV for the IP and EA, respectively, compared to the experiment [31,32]. This caused a dispute in the relativistic community, if this is due to missing electron correlation in the positive energy spectrum or due to the neglect of correlating the Dirac negative energy sea [33]. We note that the lowest $1s$ state in gold is energetically well separated from the negative energy continuum with a large gap of 941.3 keV $\approx 1.8mc^2$; from a perturbative argument, it is hard to justify that correlating negative energy states are responsible for such a large discrepancy [34]. The aim of this study is therefore to reach experimental accuracy for the ionization potential and the electron affinity of atomic gold by using a four-component relativistic formalism including contributions from the Breit interaction and QED. We note that a number of earlier good quality investigations on the IP and EA of gold have been performed; however, none has reached the level of accuracy required to determine the origin of the disagreement between experiment and theory [30,35–40].

The Hamiltonian chosen for our calculations is $H = H_{\mathrm{DC}} + H_{\mathrm{Breit}} + H_{\mathrm{QED}}$. The initial mean-field calculations were carried out using the GRASP program [41,42] in the framework of the relativistic no-virtual-pairs Dirac–Coulomb Hamiltonian (in atomic units),

$$H_{\mathrm{DC}} = \sum_i h_{\mathrm{D}}(i) + \sum_{i<j}(1/r_{ij}). \qquad (1)$$

Here, h_{D} is the one-electron Dirac Hamiltonian,

$$h_{\mathrm{D}}(i) = c\alpha_i \cdot \mathbf{p}_i + c^2\beta_i + V_{\mathrm{nuc}}(i), \qquad (2)$$

which gives Dirac–Coulomb-Hartree–Fock (DC-HF) limit values for the IP and EA using a very fine and well-converged numerical grid. Here, α and β are the Dirac matrices in the standard representation. The nuclear Coulomb potential V_{nuc} takes into account the finite size of the nucleus modeled by a 2-parameter Fermi charge distribution [43,44].

We include electron correlation via the relativistic coupled cluster method with single, double, and perturbative triple excitations [DC-CCSD(T)], as implemented in the DIRAC15 [45] program package. In these calculations, virtual orbitals with energies above 50 a.u. were omitted; all electrons were correlated down to the $1s$ level. The correlation-consistent relativistic basis sets of Dyall [46] were used, and the correlation contribution was extrapolated to the complete basis set limit using the v3z and v4z basis sets [CBS(34)]. As seen in Table I, the DC-CCSD IP and EA are lower than the experimental value, with a larger

TABLE I. Calculated IP and EA of Au at different levels of theory and error with respect to experiment [31,32] (eV).

	IP	Error	EA	Error
DC-HF	7.6892	−1.5363	0.6690	−1.6396
DC-CCSD	9.1164	−0.1092	2.1070	−0.2017
DC-CCSD(T)	9.2938	0.0683	2.3457	0.0371
DC-CCSDTQP	9.2701	0.0446	2.3278	0.0192
+Breit	9.2546	0.0290	2.3188	0.0102
+QED	9.2288	0.0032	2.3072	−0.0014
Experiment [31,32]	9.2256		2.3086	

error in the electron affinity as one would expect. Adding the perturbative triple excitation contribution overshoots the experimental mark by 68 meV and 37 meV for the IP and EA, respectively. As expected, the perturbative triples $\delta(\mathrm{T})$ contribution is significantly larger, by about 61 meV, for the electron affinity. These results clearly demonstrate that perturbative triples are insufficient to describe the electron correlation accurately despite the extrapolation to the complete basis set limit.

The next step is to estimate the effects of neglecting higher-order excitations from the valence ($5d6s$), and where possible, also from the core shells ($4f5s5p$) using Kállay's MRCC program [47–51] linked to DIRAC15. Here, we included excitations up to the full pentuple level (CCSDTQP). Because of the exponentially increasing number of Slater determinants with increasing excitation level, we needed to restrict these calculations to smaller basis sets and lower energy cutoffs for the virtual orbital space (for details, see Table II). Currently, calculations involving only up to several billions of determinants are computationally tractable by this methodology. The results are summarized in Table I and shown in more detail in Table II.

Going from perturbative to full triple excitations lowers the IP and EA by 30 and 35 meV, respectively. Accounting for quadruple excitations raises the IP by 5 meV, but has a much stronger effect of +17 meV for the EA. Finally, the pentuple (five-electron) excitations contribute less than a single meV in both cases; therefore, accounting for higher excitations is not required. We note that as we go to higher excitations, the perturbative result provides a worse approximation to the full iterative coupled cluster treatment. Thus, the highest perturbative correction used in this work (P) strongly overestimates the absolute value of the full iterative pentuple correction P, and in fact, $\delta(P)$ and δP almost cancel each other out. Taking the DC-CCSD(T) results as the starting point, the overall contribution of higher excitations amounts to −24 meV for the IP and −18 meV for EA. We can see that the CCSD(T) method, termed as the "gold standard" of electronic structure theory, although accounting for most of the electron correlation, is not sufficient to obtain meV precision. Because of the good localization of the higher excitation energy contributions in

TABLE II. Higher-order electron correlation contributions to the IP and EA of Au (eV) including basis set information and virtual space energy cutoffs (a.u.).

Contribution		IP	EA	Basis set, cutoff
δT	Valence	−0.0221	−0.0314	CBS(34), 30
	Core	−0.0074	−0.0033	v3z, 30
$\delta(Q)$	Valence	0.0048	0.0155	CBS(34), 30
	Core	0.0004	0.0019	v2z, 30 + δ(v3z, 10)
δQ	Valence	0.0010	−0.0004	v2z, 30
$\delta(P)$	Valence	−0.0014	−0.0015	v2z, 30
δP	Valence	0.0009	0.0013	v2z, 5
Total		−0.0237	−0.0179	

TABLE III. QED contributions to the IP and EA of Au (eV).

		IP		EA	
		DC-HF	δCCSD	DC-HF	δCCSD
SE	SZE	−0.0213		−0.0079	
	LGO	−0.0272		−0.0117	
	ENLO	−0.0264		−0.0114	
	MLSO	−0.0261	−0.0070	−0.0112	−0.0039
VP	GRASP	0.0053		0.0023	
	MLSO	0.0049	−0.0002	0.0021	−0.0001
SEVP	MLSO	0.0000	0.0026	0.0000	0.0015
Total	MLSO	−0.0212	−0.0046	−0.0091	−0.0025

the valence-shell region (see Table II), instead of using the computationally cumbersome and demanding all-order coupled cluster contributions, in practice, it is more appropriate to use some efficient "dressed valence-complete CI" approach that includes potentially exact correlation of the valence electrons and thus, captures the majority of the effect of the higher excitations. Examples of such efficient size-extensive valence-shell approaches are the intermediate Hamiltonian or equation-of-motion coupled cluster methods (see Ref. [52] for a comprehensive review of coupled cluster approaches).

We now turn our attention to the treatment of the Breit and QED contributions. The lowest order relativistic correction to the Dirac Hamiltonian is the Breit operator [53] in the Coulomb gauge between electron 1 and 2,

$$B_{12} = -\frac{\vec{\alpha}_1 \vec{\alpha}_2}{r_{12}} \exp(ic^{-1}|\omega_{12}|r_{12})$$
$$- (\vec{\alpha}_1 \vec{\nabla}_1)(\vec{\alpha}_2 \vec{\nabla}_2) \frac{\exp(ic^{-1}|\omega_{12}|r_{12}) - 1}{c^{-2}\omega_{12}^2 r_{12}}, \quad (3)$$

where ω_{12} is the frequency of the exchange photon between the two electrons. We used the Breit term variationally in the low frequency limit ($\omega_{12} \to 0$) within a Fock-space coupled cluster approach (DCB-FSCCSD), using the Tel Aviv atomic computational package [54]. The finite frequency contribution to the Breit term was calculated perturbatively at the DC-HF level as implemented in GRASP. This contribution, however, amounts to less than 1 meV in both cases. Table I shows that the overall effect of the Breit contribution lowers the calculated IP by 15 meV, and the EA by 9 meV.

To account for the QED corrections to the IP and EA, we applied the model Lamb shift operator (MLSO) of Shabaev and co-workers [55] to the atomic no-virtual-pair many-body DCB Hamiltonian as implemented into the QEDMOD program. This model Hamiltonian uses the Uehling potential and an approximate Wichmann–Kroll term for the vacuum polarization (VP) potential [25], and local and nonlocal operators for the self-energy (SE), the cross terms

(SEVP), and the higher-order QED terms [22]. Our implementation of the MLSO formalism into the Tel Aviv atomic computational package allows us to obtain the VP and SE contributions beyond the usual mean-field level, namely at the DCB-FSCCSD level. The individual QED contributions are presented in Table III. To test the validity of these results, we also carried out perturbative QED calculations using the Uehling and Källén–Sabry [25,56] terms (as implemented in GRASP) for the VP, and the effective nonlocal SE operator (ENLO) originally introduced by Ginges and Flambaum [23], and modified and implemented by our group into GRASP [24]. The two approaches (ENLO and MLSO) give similar results at the mean-field level. For comparison, we also include the more approximate perturbative SE values obtained by using the screened Z-expansion (SZE) interpolating the tabulated values for hydrogenlike systems reported by Mohr [57–59] and by using the local Gaussian-type operator (LGO) of Pyykkö [60]. For the final QED contributions, we use the MLSO values. The overall Lamb shift of the ionization potential is −26 meV, with the CC contribution accounting for about 21%, which is an improvement over the estimated QED contributions of Pyykkö and Labzowsky (ranging between −18 and −26 meV) [20,61]. In case of the EA, the overall Lamb shift is only half in size compared to the IP, but the relative CC contribution remains the same. This clearly indicates that electron correlation contributions to QED cannot be neglected. Note that the overall QED contributions are of the same magnitude as the higher-order electron correlation contributions.

Adding all the contributions provides us with calculated IP and EA just 3.2 and 1.4 meV off the corresponding experimental values, respectively (Table I). Comparing our final results to the earlier theoretical values obtained from accurate electron correlation treatments in Table IV, we find that nearly all previous results are considerably lower than experiment. One exception is the DC-CI+MBPT2 calculation for the gold EA, where the excellent agreement with experiment is attributed to the empirical scaling of the electron correlation to simulate higher-order correlation effects [39].

TABLE IV. Calculated IP and EA of gold (eV) compared with earlier theoretical studies.

Method	References	IP	EA
Experiment	[31,32]	9.2256	2.3086
DC-CCSDTQP +Breit + QED	this work	9.2288	2.3072
DKH2-MRCISD	[36]	9.04	2.11
DKH2-ACPF	[36]	9.08	2.28
DCB-FSCCSD	[30]	9.086	2.269
DKH2-CCSD(T)	[35]	9.123	2.229
DC-CI + MBPT2	[39]		2.3070
PP-CCSD(T)	[37]	9.13	2.22
DCB-MSIH	[38]	9.2076	
EOM-CCSD	[40]	9.2103	

Through highly accurate theoretical treatment of the gold atom accounting for all contributions beyond the standard relativistic coupled cluster approach, our results resolve a long-standing debate about the origin of the discrepancy between theory and experiment. We expect that the electron correlation contribution from the negative energy states will be of the order of 1 meV or less, but should be included in future investigations together with an explicit treatment of the QED Feynman diagrams within a more accurate electron correlation framework such as the R12 methodology [62]. We add the important conclusion that in order to obtain balanced and precise results higher-order correlation effects and Breit and QED contributions (preferably at the correlated level) must be included simultaneously; neglecting any of them from the computational scheme renders the inclusion of others meaningless.

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