Semiclassical formulation of term energies and electrostatic intervals in He I

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A semiclassical core-polarization-penetration model has been used to parametrize energy-level and energy-interval data for He I. Various contributions to the energy of the form $\langle \gamma r^{-s} \rangle$ with $s \leq 10$ were tested in attempts to account for different types of polarizabilities, dynamical correlations, and relativistic and retardation effects, which are all exactly calculable for the hydrogenlike core. Penetration effects were simulated by replacing expectation values by time averages over classical Kepler orbits that penetrate a parametrized hollow shell of core charge. It was found that the best fits were obtained if only dipole, quadrupole, lowest-order dynamical correlations, and relativistic mass corrections to the gross energy were included, and that higher-order polarizabilities and retardation effects worsened the fit. The approach generally reproduces observed $J=L$ singlet-triplet averages to within experimental uncertainties for $n \geq 5$ and $l \geq 2$. Three free parameters each are necessary to describe the D and F Rydberg series, whereas the $l \geq 4$ series can be described with no free parameters. The model can be very precisely tested with the use of available microwave-optical resonance data for the $\Delta n = 0$ F-G-H-I intervals, for which the relativistic and polarization energies have been observed directly.

I. INTRODUCTION

The parametrization of high n and l states in multielectron atoms through their modeling as a single electron in the electric field of a deformable core of charge can provide a very precise description of a large amount of information (either experimental or theoretical) in terms of a small number of physically interpretable parameters.[1] Through the exploitation of semiempirical trends in these parameters, extrapolations and interpolations can be made for members of a Rydberg series, an isoelectronic sequence, or a homologous system. This formulation is particularly useful for two-valence-electron spectra, where the very large core polarizabilities arising from the single out-of-shell core electron strongly break the hydrogenic l degeneracies, leading to well-separated and easily recognized groups of lines applicable to calibration and diagnostic purposes. However, differences between theoretically computed and experimentally deduced polarizabilities and nonadiabatic correlations have been noted in the helium,[2-7] beryllium,[8] and magnesium[8] isoelectronic sequences. These differences could arise from the neglect of higher-order contributions to the polarizabilities and nonadiabatic corrections, core-penetration effects, or exchange effects. Alternatively, they could merely indicate that this simple model is not capable of describing the system. The standard semiempirical core polarization describes only long-range interactions, but a semiclassical extension of the model[9] that includes penetration effects has shown some success in accounting for short-range interactions. Since the polarization model is used extensively in high-precision spectroscopic studies it is worthwhile to explore its empirical validity.

The neutral helium atom is the simplest example to which the core-polarization model can be applied, and permits a very stringent test of that application. For He I, the polarizabilities and nonadiabatic correlations of the hydrogenlike core are exactly calculable to arbitrary order[6,10-14] and precise measurements have been made of $\Delta n = 0$ intervals between F, G, H, and I states using microwave-optical resonance techniques.[15,16] These experiments directly observe the relativistic and polarization energies exclusive of the much larger gross energy, and thus provide the best available test of the reliability of the polarization model. In addition, sophisticated *ab initio* calculations are available for the lower l states, and bibliographic citations to these calculations can be found in Refs. 16 and 17. Since the goals here are to test the accuracy of the polarization model for parametrizing empirical data and to search for empirical regulari-

ties, our approach is separate from, but complementary to, *ab initio* theory.

For the reasons described above, it is possible to fit a very detailed version of the polarization model to available He I data, including various orders of multipole moments and nonadiabatic correlations, core-penetration effects, and even retardation contributions[18] to see whether the model is improved, worsened, or insensitive to these inclusions. Previous attempts[5] to improve the reliability of this model have involved the replacement of the hydrogenlike theoretical adiabatic and nonadiabatic polarizabilities by free parameters determined empirically from the observations. Unfortunately, this approach has been found to infer different polarizability parameters for each Rydberg series. We have utilized an alternative procedure, in which the various polarizability quantities are fixed at their theoretical values and core penetration is parametrized for each Rydberg series using a classical model[9] employing Kepler orbits that penetrate a hollow shell of charge. Since the penetration decreases with increasing l, this approach should permit reliable predictions for high n and l.

This parametrization is valuable in the study of the helium atom, since the empirical regularities can expose inconsistencies and provide extremely accurate predictions for large numbers of states with minimal calculational effort, often to accuracies equivalent to those of the available data. However, the study is not intended as a substitute for the precise *ab initio* calculations which are possible for He I, but rather as means of refining the model and determining its reliability in applications to more complex atoms, for which experimental precision greatly exceeds that of *ab initio* theory.

II. SEMICLASSICAL POLARIZATION-PENETRATION MODEL

The spinless (or suitably spin-averaged) term energy T of an active electron of principal and angular-momentum quantum numbers n and l, orbiting with a coordinate r measured from the center of a deformable core of charge ζ, can be written as[9,10]

$$T=R\left[\langle\zeta r^{-1}\rangle+\alpha^2(\langle\zeta^2 r^{-2}\rangle-\tfrac{3}{4}\langle\zeta r^{-1}\rangle^2)+\sum_{k=4}^{k_{\max}}\langle\xi_k r^{-k}\rangle\right]. \quad (1)$$

In Eq. (1) R is the reduced-mass-corrected Rydberg constant (for a He^+ core, 109 722.2740 cm^{-1} or 3 289 391 023 MHz/c), α is the fine-structure constant (1/137.035 96), ζ is in units of e, r is in units of the reduced-mass-corrected Bohr radius a_0, and ξ_k is in units a_0^{k-1}. The first contribution on the right-hand side is the nonrelativistic gross energy (written in this form through use of the virial theorem) and the second contribution is the relativistic correction to the kinetic energy. The ξ_k quantities can include several different types of physical processes. One type involves electrostatic interactions arising either directly or indirectly from the polarizability of the core.[10] These contributions can be described by a separate series in reciprocal powers of r for each order of a perturbation expansion based upon the number of intermediate virtual states included.[11,12] The second-order perturbation can be interpreted as a sum over the standard dipole, quadrupole, octupole, etc., polarizabilities of the core alone, whereas third- and higher-order perturbations involve more complicated mutual polarizations of both the core and outer electron distributions. Another type of interaction concerns nonadiabatic dynamical correlations,[2,6,13,14] which account for the inability of the core to instantaneously adapt to the motion of the outer electron. The second-order perturbations and the nonadiabatic correlations for the He I system were computed for $k \leq 6$ already in 1934 by Ludwig.[2] A general formula for the nonadiabatic correlations for arbitrary k has been given by Deutsch[6] (see footnote f of Table I), and calculations through fourth-order perturbations for $k \leq 10$ have been made by Dalgarno and Lewis[12] for H_2^+, which can be applied (with appropriate sign changes) to a He^+ core. It has also been suggested[18] that retardation effects arising from the motion of the outer electron and the finiteness of the speed of light might make small contributions to the energy. Table I lists the theoretical values for $k=4-10$ for second, third, and fourth orders of adiabatic polarizabilities[12] and nonadiabatic dynamical correlations,[6] as well as retardation effects[18] for $k \leq 6$, all for nuclear charge Z.

The quantities ζ, ζ^2, and ξ_k (generically designated henceforth as γ) have been left inside the averages $\langle\gamma r^{-s}\rangle$ since their values will depend upon r if penetration occurs. If penetration is negligible, the γ quantities can be factored outside the averages and $\langle r^{-s}\rangle$ can be replaced by its hydrogenlike value.[19] For the quantum-mechanical problem it is not possible to neglect penetration ef-

TABLE I. Hydrogenlike values for ξ_k coefficients in Eq. (1) for $k=4$ to 10.

	$Z^k\xi_k$					
	Second order[a]	Third order[b]	Fourth order[a]			
k	Adiabatic Perturbations			Nonadiab.[c]	Retard.[d]	Total
4	$\frac{9}{2}$					$+\frac{9}{2}$
5					$(-99\alpha Z/4\pi)$	0
6	15			$-\frac{129}{4}$	$(\frac{129}{4})$	$-\frac{69}{4}$
7		$-\frac{213}{2}$				$-\frac{213}{2}$
8	$\frac{525}{4}$		$\frac{3555}{32}$	$-\frac{1605}{8}$		$+\frac{1335}{32}$
9		-1773				-1773
10	$\frac{2835}{4}$[e]		$\frac{80379}{8}$[e]	$-\frac{22855}{8}$[f]		$+\frac{31597}{4}$

[a]Dalgarno and Lewis, Ref. 12.
[b]Dalgarno and Lewis, Ref. 12, with a negative sign to convert the result from H_2^+ to He.
[c]Deutsch, Ref. 6.
[d]Kelsey and Spruch, Ref. 18 (not included in the total).
[e]The sum of the second- and fourth-order contributions for $k=10$ given in Ref. 12 agrees with the corresponding combined values obtained by another method in Ref. 10. However, it should be noted that the second-order $k=10$ contribution in Ref. 12 is $\frac{1}{3}$ the value obtained by the general formula given in Refs. 6 and 11.
[f]Obtained from Eq. (19) of Ref. 6 (1970), which must be divided by two to agree with the $k=6$ and 8 values given in the same paper.

fects for $k>2l+2$, since the integrand in the expectation values then has a pole at the origin. This is evidenced by the fact that the hydrogenlike expectation values diverge for $k>2l+2$. In these cases the integral is dominated by the region inside the core, where ξ_k is assumed to vanish, so the model requires a truncation of the sum above $k=2l+2$. The higher reciprocal powers with $k\leq 2l+2$ will also tend to be reduced by penetration effects and, since Table I suggests the onset of alternations of the sign of ξ_k with increasing k, it may be possible to partially include penetration effects simply by truncating the sum at some $k_{\max}<2l+2$ on the basis of agreement with experimental observations. It is well known[12,20] that this type of formulation of long-range forces as a power-series expansion in the reciprocal of the separation is divergent and must be appropriately truncated. As will be discussed below, best agreement with currently available data was obtained if the sum was truncated above $k=6$ and retardation corrections were excluded.

In cases where explicit inclusion of penetration effects is desired, the average values $\langle \gamma r^{-s}\rangle$ will, for purposes of this classical model, be interpreted as the classical analogs of the quantum-mechanical expectation values, which are time averages over the quantized Kepler orbits. The core is modeled as a hollow spherical shell of radius ρ with a charge $-\Delta\zeta$ distributed uniformly over its surface. It is further assumed that the various moments and nonadiabatic correction factors vanish inside this shell of charge. Clearly a volume distribution of charge would be a more realistic model, but this would sacrifice the calculational simplicity of an elliptical internal orbit. As a compromise, a hollow shell is used which has an n-independent radius, but the surface charge is allowed to grow weakly with the depth of orbit penetration. A relationship that has been found to fit the data quite well is

$$\Delta\zeta=\Delta\zeta_0\exp(B/P)\,, \tag{2}$$

where $\Delta\zeta_0$ and B are empirical constants, P is the perihelion as computed from the external orbit

$$P=(1-\epsilon)n^2/\zeta\,, \tag{3}$$

and ϵ is the eccentricity of the orbit

$$\epsilon=[1-l(l+1)/n^2]^{1/2}\,. \tag{4}$$

The desired averages in Eq. (1) can then be computed by separating the orbital integral into internal and external segments

$$\langle \gamma r^{-s} \rangle = \frac{\int_{r<\rho} dt\, \gamma r^{-s} + \int_{r>\rho} dt\, \gamma r^{-s}}{\int_{r<\rho} dt + \int_{r>\rho} dt} . \quad (5)$$

Conservation of energy and angular momentum relate the major axes and eccentricities of the internal and external orbits to ρ and $\Delta\zeta$, and the integrals can be reduced to elementary forms using Kepler's three laws. Details of this calculation can be found in Ref. 9.

III. EFFECTIVE ELECTROSTATIC CONFIGURATION AVERAGES

A semiclassical electrostatic model cannot be expected to account for spin-associated interactions such as magnetic fine-structure and exchange effects. Therefore it is desirable to define some type of "spinless" average over the configuration manifold which minimizes these nonelectrostatic contributions and still retains some empirical predictive meaning. For a two-electron system with spin-orbit magnetic interactions only, the exchange and magnetic contributions vanish from the quantity[9]

$$\bar{T} = [T(^1L_l) + T(^3L_l)]/2 + [T(^3L_{l+1}) - T(^3L_{l-1})]/2(2l+1) . \quad (6)$$

Unfortunately this expression is not applicable to He I, both since spin-spin, orbit-orbit, and spin-other-orbit contributions are substantial, and since the states cannot strictly be classified according to spin multiplicity, being admixtures of singlet and triplet wave functions.[21] Cok and Lundeen[16] have attempted to construct a quantity analogous to Eq. (6) for He I by using theoretically computed magnetic and exchange contributions to reduce the experimental interval manifolds to a single electrostatic spinless interval, which they then compare with their theoretical calculation for the direct electrostatic fine structure. Their procedure utilizes hydrogenic calculations for the magnetic fine structure,[22] which exhibit residual discrepancies of up to five times the quoted standard deviations in the measurements for the F and G manifolds, and of up to 50 times the corresponding figures for the D manifolds. These anomalies clearly do not form a satisfactory basis for the definition of quantities that are to be used for semiempirical predictions. Some authors[3,7] have reduced the configuration manifolds by computing the statistically weighted centroid, but this average removes neither exchange nor magnetic contributions. For purposes of this study we have chosen to consider the quantity

$$\bar{T} = [T(^1L_l) + T(^3L_l)]/2 , \quad (7)$$

which is well-defined experimentally, and, in the limit of small magnetic fine structure, removes exchange effects. The error encountered in this procedure will be of the order of magnitude of the fine-structure interval.

IV. DATA SOURCES AND ANALYSIS

Our goal was to accurately describe observed high n and l states in He I using Eqs. (1)–(5) through a weighted nonlinear least-squares adjustment[23] of the penetration parameters ρ, $\Delta\zeta_0$, and B, and a suitable selection of $k_{\max}$. The uncertainties in the absolute specifications[4] of the ground state and the ionization potential of He I are, respectively, ± 0.15 cm^{-1} (± 4500 MHz) and ± 0.02 cm^{-1} (± 600 MHz), which are much larger than the uncertainties of many of the observed transition intervals. In addition, the precision of the values[24] of the Rydberg constant (0.005 ppm) and the speed of light (0.004 ppm) contribute an uncertainty of ± 20 MHz to the computation of the gross energy. To avoid introducing these uncertainties into the more accurately determined relative energy intervals, several procedures were investigated. One approach was to treat the ionization potential as an additional fitting parameter, evaluated separately for each Rydberg series. Another approach was to fit differences in term values within each Rydberg series, whereas a third approach was to fit energy differences in term values between two transition-coupled Rydberg series. The results of the first two approaches clearly indicated that each Rydberg series would require its own set of penetration parameters, but that the G, H, and I series were, to within the accuracies in existing data sources, free of penetration effects. It became clear that the microwave-optical resonance data[15,16] were vastly superior in precision for determination of these small effects and that a satisfactory analysis could be obtained by fitting them alone. For these $\Delta n = 0$ intervals the gross energies (which are $10^4 - 10^5$ times larger than the polarization energies) do not enter and the polarization and relativistic energies are specified directly.

The data listed in Table II were fitted by nonlinear least-squares methods[23] using Eq. (1) with $k_{\max}$ set at values from 4 to 10, including or ex-

TABLE II. Nonlinear least-squares fits of penetration parameters to $\Delta n = 0$ intervals measured by microwave-optical techniques.

Transition	Energy interval (MHz) Observed[a]	Fitted − observed
7*D*-7*F*	38 309.90(96)	+ 1.11
8*D*-8*F*	25 848.57(21)	−0.51
9*D*-9*F*	18 242.32(12)	+ 0.08
10*D*-10*F*	13 344.86(12)	+ 0.82
11*D*-11*F*	10 051.68(15)	+ 1.46
7*F*-7*G*	5 738.35(99)	−0.04
8*F*-8*G*	3 899.34(50)	+ 0.06
9*F*-9*G*	2 766.12(24)	0.00
10*F*-10*G*	2 031.00(56)	−0.05
11*F*-11*G*	1 533.86(58)	−0.03
7*G*-7*H*	1 359.16(11)	−1.68
8*G*-8*H*	931.34(44)	+ 0.22
7*H*-7*I*	402.8(47)	+ 20.6

[a] *D-F* and *F-G* are from Ref. 15, *G-H* and *H-I* are from Ref. 16. Experimental uncertainties in the quantities [as defined in Eq. (7)] are listed in parentheses.

cluding either or both the $k = 5$ and $k = 6$ retardation contributions. The fits for all four sets of intervals were best (in the χ^2 sense) if the sum was truncated above $k = 6$ and the retardation contributions were omitted. The *G*, *H*, and *I* data are sparse, but seem to clearly indicate that penetration can (except for its role in the $k > 6$ truncation) be neglected for these states at present accuracies. The measured 7*H*-7*I* interval is, however, 20 MHz lower than the prediction and presents a slight challenge to this model. However, Ref. 16 points out that it was necessary to correct for a power shift of about 12 MHz for this interval, leading to much higher uncertainties (± 4.7 MHz) than for the other cases. It can also be clearly seen in Fig. 6 of Ref. 16 that the measured value for 7*H*-7*I* deviates significantly from the trend of *D-F*, *F-G*, and *G-H* measurements, and an independent measurement with reduced uncertainties would be helpful in resolving this question. Having established that the *G* levels were nonpenetrating, it was possible to fit the *F-G* intervals by adjusting only the *F* penetration parameters, and, in turn, to fix them so as to fit the *D-F* intervals by adjusting only the *D* penetration parameters. A comparison between fitted results and observations is given in Table II and the values for the fitted parameters are given

TABLE III. Model parameters for describing data in Table II by Eqs. (1)–(5).

γ	$r < \rho$	$r > \rho$
ζ	$1 + \Delta\zeta$	1
ξ_4	0	$\frac{9}{32}$
ξ_5	0	0
ξ_6	0	$-\frac{69}{256}$

$k_{max} = 6$,
$\rho(D) = 8.971$, $\Delta\zeta(D) = (1.897 \times 10^{-4})\exp(9.124/P)$,
$\rho(F) = 6.949$, $\Delta\zeta(F) = (4.217 \times 10^{-5})\exp(16.34/P)$,
$\rho(G) < 10$, $\rho(H) < 15$, $\rho(I) < 21$.

in Table III. These values for ρ, $\Delta\zeta_0$, and B were then used to compute the term values for the *D*, *F*, and *G* Rydberg series, and the results are compared with available observations[4] in Table IV. Since the term values are specified relative to the ionization potential, there is an inherent uncertainty of ± 0.02 cm^{-1} in these series, although individual intervals have higher precisions.

It is interesting that, subsequent to the original submission of our manuscript, revised spinless intervals were reported by Cok and Lundeen[22] that agree much better with our data than their original estimates. This clearly illustrates the advantages of semiempirical calculations.

V. CONCLUSION

The results indicate that this semiclassical polarization-penetration model is sufficient to describe currently available energy-level data in He I for $l \geq 2$, and thus provides a basis for reliable extrapolations. It also indicates that contributions to the core polarization of higher order than dipole and quadrupole are not only unnecessary, but worsen agreement with observations. This result is classically plausible, since higher reciprocal powers of r emphasize the near region, and their contributions could be suppressed by penetration effects which would be negligible for lower reciprocal powers. This lends credence to the practice[1] of parametrizing polarization effects in many-electron atoms by including only effective dipole and quadrupole polarizability contributions. The analysis also indicates that the lowest nonadiabatic correction (which combines with the quadrupole polarizability to give a negative coefficient for r^{-6}) should definitely be included, although apparent

TABLE IV. Term values computed from fit to $\Delta n = 0$ intervals.

Level	$1+\Delta\zeta$	Term values (cm^{-1}) Observed[a]	Computed − observed
3*D*	1.002 09	12 207.40	+ 1.18
4*D*	1.002 89	6 865.19	+ 0.10
5*D*	1.003 27	4 392.94	+ 0.02
6*D*	1.003 48	3 050.25	0.00
7*D*	1.003 60	2 240.78	−0.01
8*D*	1.003 69	1 715.40	+ 0.05
9*D*	1.003 75	1 355.36	−0.03
10*D*	1.003 79	1 097.78	−0.02
11*D*	1.003 82	907.21	−0.01
4*F*	1.000 33	6 858.78	0.00
5*F*	1.000 44	4 389.54	0.00
6*F*	1.000 50	3 048.24	0.00
7*F*	1.000 54	2 239.51	−0.02
8*F*	1.000 56	1 714.43	+ 0.05
9*F*	1.000 58	1 354.75	−0.03
10*F*	1.000 59	1 097.33	−0.01
11*F*	1.000 60	906.87	0.00
5*G*	1.0	4 389.03	+ 0.02
6*G*	1.0	3 047.92	+ 0.02

[a]Reference 4, averaged as Eq. (7).

positive coefficients of r^{-6} can occur in a simple polarization analysis as the result of penetration effects if l is not sufficiently high. This may have implications for the Be and Mg isoelectronic sequences, where nonpenetrative core-polarization analyses yield positive coefficients for r^{-6} despite theoretical indications that the negative dynamical correlations should prevail.[8,25] The inclusion of the retardation corrections also worsened the penetration fits and the agreement for the unpenetrated levels, but these states are probably not of sufficiently high n to provide an adequate test of this type of interaction.

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