# Upper and Lower Bounds to Atomic and Molecular Properties. II. Electric Polarizabilities of Four-Electron Atoms by a Lower-Bound Procedure

James S. Sims and John R. Rumble, Jr.

*Department of Chemistry, Indiana University, Blomington, Indiana 47401*

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Wave functions, which include interelectron coordinates $r_{ij}$ explicitly, are employed for the $1s^2 2s^2\,{}^1S$ and $1s^2 2s 2p\,{}^1P_1$ states of Be I, C III, and O V in obtaining lower bounds and Hylleraas variation-perturbation estimates of dipole polarizabilities for the lowest $^1S$ states of Be I, C III, and O V. Interpolation techniques are used to make a graphical study of the polarizability behavior along the entire isoelectronic sequence. The results of this study are polarizabilities for the lowest $^1S$ state of Be I with probable accuracy $\leq 2\%$, and the rest of the isoelectronic sequence with probable accuracy of $(2-5)\%$.

## I. INTRODUCTION

The ultimate goal of any quantum-chemical calculation must be the accurate prediction of an experimentally measurable property. The static dipole polarizability, which describes the redistribution of the electronic charge cloud in the presence of an electric field, is one of the most interesting and useful properties of an atom (or atomic ion). To date, reliable values of the polarizabilities of most atoms are not yet available. On the experimental side, experimental values are often clouded by defects in the theories by which the experimental data are interpreted, as well as by various uncertain environmental effects. For Be, no experimental value exists. On the theoretical side, the electronic distortion involves virtual transitions to an infinite manifold of states, and thus cannot be described in terms of a single unperturbed eigenfunction. Thus existing quantum-mechanical procedures[1] yield disparate results, sometimes even with two varieties of a single method.[2] Thus there is a need for calculated polarizabilities of convincing reliability. An interesting new procedure has recently been described by Weinhold[3] (and applied to two-electron atoms)[4] which gives a *rigorous upper bound* to the second-order energy (and thus, a *lower bound* to the electric polarizability) within a variational formulation in which one may systematically improve the rigorous bounds to any desired extent. We report herein application of this method to the ground states of Be I, C III, and O V and extend these results to higher members of the Be isoelectronic sequence. The wave functions employed in this work represent the best variational wave functions available (on an energy criterion) for the lowest states of $^1S$ and $^1P$ symmetry for Be I, C III, and O V.

## II. THEORY

When an unperturbed atom, described by

$$\mathcal{H}_0 \psi_k^{(0)} = E_k^{(0)} \psi_k^{(0)} , \tag{1}$$

is placed in a static electric field (associated with the perturbation operator $V$), the resulting Schrödinger equation

$$(\mathcal{H}_0 + FV)\Psi_k = \epsilon_k \Psi_k \tag{2}$$

is usually solved by developing the eigenfunction and eigenvalue in a perturbation series,

$$\Psi_k = \psi_k^{(0)} + F\psi_k^{(1)} + F^2 \psi_k^{(2)} + \cdots$$

$$\epsilon_k = E_k^{(0)} + F E_k^{(1)} + F^2 E_k^{(2)} + \cdots ,$$

according to the powers of the field strength $F$.[3] Here, in the dipole approximation, the perturbative interaction $V$ is

$$V = \sum_{i=1}^{N} z_i , \tag{3}$$

where $z_i$ is the component of the radial coordinate $r_i$ in the field direction, the unperturbed operator $\mathcal{H}_0$ is, in the nonrelativistic approximation,[5]

$$\mathcal{H}_0 = \sum_{i=1}^{N} \left( -\tfrac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j=1}^{N} \frac{1}{r_{ij}} , \tag{4}$$

and $E_k^{(0)}$ and $\psi_k^{(0)}$ are the energy eigenvalue and corresponding wave function for the $k$th unperturbed electronic state. From the equations that the perturbative corrections $\psi_k^{(n)}$ to the wave function are found to satisfy, when the perturbed eigenfunction $\Psi_k$ and eigenvalue $\epsilon_k$ are expanded as a power series in $F$, we obtain

$$F_k^{(1)} = \langle \psi_k^{(0)} | V | \psi_k^{(0)} \rangle \tag{5}$$

and

TABLE I. Computed values for Be I, C III, O V[a].

| Configs. | | $\epsilon (\times 10^2)$ | $E(^1S)$ | $E(^1P)$ | $S_{a-}$ | $\alpha-$ | $\alpha_{VP}$ |
|---|---|---|---|---|---|---|---|
| $^1S$ | $^1P$ | | | | | | |
| **Be I** | | | | | | | |
| $46 \times 18$ | | 14.266 | $-14.66155$ | $-14.44317$ | 0.98977 | 11.48 | 33.51 |
| | | | | | | (1.702) | (4.966) |
| $89 \times 53$ | | 2.2317 | $-14.666485$ | $-14.47246$ | 0.99975 | 35.4135 | 36.58 |
| | | | | | | (5.247) | (5.421) |
| $105 \times 53$ | | 1.6470 | $-14.666546$ | $-14.47246$ | 0.99986 | 35.75 | 36.56 |
| | | | | | | (5.297) | (5.418) |
| **C III** | | | | | | | |
| $89 \times 53$ | | 2.2158 | $-36.53337$ | $-36.06283$ | 0.99975 | 3.4885 | 3.6405 |
| **O V** | | | | | | (0.5175) | (0.5401) |
| $89 \times 53$ | | 3.0726 | $-68.40957$ | $-67.68433$ | 0.99953 | 0.9833 | 1.026 |
| | | | | | | (0.1462) | (0.1526) |

[a] Wave functions and definitions of quantities are given in Paper I (Ref. 6). Values are in atomic units except for values in parentheses, which are in units of $\text{Å}^3$.

$$E_k^{(2)} = \langle \psi_k^{(0)} | V - E_k^{(1)} | \psi_k^{(1)} \rangle . \tag{6}$$

The static (dipole) polarizability $\alpha_k$ of state $k$ is defined formally as

$$\alpha_k = -\left( \frac{\partial^2 \epsilon_k}{\partial F^2} \right)_{F \to 0} , \tag{7}$$

and can be connected with the second-order perturbation energy $E_k$ by the relation

$$\alpha_k = -2 E_k^{(2)} . \tag{8}$$

However, Eq. (6) is of little practical value in obtaining $E_k^{(2)}$, and consequently $\alpha_k$, since neither the unperturbed eigenfunction $\psi_k^{(0)}$ nor the first-order correction $\psi_k^{(1)}$ is generally available.

Weinhold[3] has recently described an alternative theoretical procedure which gives a *rigorous upper bound* to the second-order energy (and thus a *lower bound* to the electric polarizability) even when both $\psi_k^{(0)}$ and $\psi_k^{(1)}$ are unknown. One may introduce variational approximations to both $\psi_k^{(0)}$ and $\psi_k^{(1)}$ and thereby systematically improve the rigorous bound to any desired extent. To obtain his result, Weinhold obtains an upper bound to the second-order perturbation when the exact but unknown eigenfunctions $\psi_k^{(0)}$ and $\psi_k^{(1)}$ are replaced by their variational approximations $\varphi_k^{(0)}$ and $\varphi_k^{(1)}$. For the cases we are considering, namely, $^1S$ states of the beryllium isoelectronic sequence, the atomic inversion symmetry ensures that $\psi_k^{(0)}$ and $\psi_k^{(1)}$ are of opposite parity, so that the first-order energy correction $E_k^{(1)}$ [Eq. (5)] vanishes identically, and Weinhold's formula becomes[4]

$$\alpha \geq 2 \frac{[-S\langle \varphi^{(0)} | V | \varphi^{(1)} \rangle - \epsilon (\langle \varphi^{(1)} | V^2 | \varphi^{(1)} \rangle - \langle \varphi^{(0)} | V | \varphi^{(1)} \rangle^2)^{1/2}]^2}{\langle \varphi^{(1)} | \mathcal{H}_0 - E^{(0)} | \varphi^{(1)} \rangle} \tag{9}$$

where we have suppressed the subscript $k$, which labels a particular electronic state.

In Eq. (9), $S = \langle \varphi_k^{(0)} | \psi_k^{(0)} \rangle$ is the overlap of the approximate and true unperturbed eigenfunctions, both $\psi_k^{(0)}$ and $\varphi_k^{(0)}$ are assumed to be normalized, and

$$\epsilon = (1 - S^2)^{1/2} . \tag{10}$$

The approximations $\varphi^{(0)}$ were taken to be the $^1S$ wave functions described in Paper I[6] of this series, i.e., $\varphi^{(0)} = \psi_\gamma(^1S)$. The approximations $\varphi^{(1)}$ were taken to be linear trial functions of the same form as the $^1P$ wave functions of Paper I, viz., $\varphi^{(1)}$

$= \sum_k C_k^{(1)} \Phi_k^{(1)}$, where the $\Phi_k$ are the $^1P$ configurations of Paper I. Because of the close connection between Eq. (9) and the Hylleraas variation-perturbation method,[4] the trial $\varphi^{(1)}$ was taken to be just the function obtained in the Hylleraas procedure. This corresponds specifically to the choice[7]

$$C_k^{(1)} = \sum_I \Omega_{kI} \langle \Phi_I^{(1)} | V | \varphi^{(0)} \rangle , \tag{11}$$

where $\vec{\Omega} = \{\Omega_{kI}\}$ is the inverse of the matrix with elements $\langle \Phi_k^{(1)} | E^{(0)} - \mathcal{H}_0 | \Phi_I^{(1)} \rangle$. In the Hylleraas procedure the calculated $E_k^{(2)}$ is known to be ex-

tremely sensitive to the choice of field-free wave function $\varphi_k^{(0)}$, but relatively insensitive to the corrections $\varphi_k^{(1)}$.[4]

Equation (9) becomes, in the notation of Paper I,

$$\alpha \geq \frac{8\pi}{3} \frac{[-S_a - |\bar{W}_0| - \epsilon_{a+}(\langle\varphi^{(1)}|W^2|\varphi^{(1)}\rangle - |\bar{W}_0|^2)^{1/2}]^2}{\langle\varphi^{(1)}|\mathcal{H}_0 - E^{(0)}|\varphi^{(1)}\rangle} . \tag{12}$$

Here

$$|\bar{W}_0| \equiv \langle\varphi^{(0)}|V|\varphi^{(1)}\rangle, \tag{13}$$

and $W^2 = (\tfrac{3}{4}\pi)X_0^2$. All numerical values needed for the evaluation of $\alpha$ can thus be obtained from the results of Paper I; they are collected in Table I, along with the lower bound to $\alpha(\alpha-)$ computed in this work. From Eqs. (8) and (12) we obtain in the limit $S \to 1$ the familiar Hylleraas variation-perturbation (VP) result[7,8]

$$E_k^{(2)} \approx \frac{\langle\varphi_k^{(0)}|V|\varphi_k^{(1)}\rangle^2}{\langle\varphi_k^{(1)}|E_k^{(0)} - \mathcal{H}_0|\varphi_k^{(1)}\rangle} . \tag{14}$$

Equation (14) is employed to obtain the conventional variation-perturbation result (listed as $\alpha_{VP}$ in Table I.). This value is no longer a rigorous bound,[4,9] but the agreement between the values obtained by this result and the rigorous result may be taken as a rough measure of convergence in the calculations.

## III. RESULTS

Lower bounds to polarizabilities were calculated for the lowest $^1S$ state of Be I, C III and O V. The results of our calculations are tabulated in Table I and compared with previous calculations in Table II. In Table I we include the conventional variation-perturbation (VP) result obtained from the final 105-term (or 89-term) $\varphi^{(0)}$ and 53-term $\varphi^{(1)}$. This value is no longer a rigorous bound, but since the result is the most extensive available and supercedes previous similar estimates, we give it in Table II as our recommended value and take the agreement between this value and the computed rigorous lower bound as a measure of the convergence in the calculations.

It appears from Table I that the bounds have converged quite well (~2% except for O V). However, inspection of the various Be I calculations indicate that the VP result is probably of high accuracy (≤2%). This conclusion is supported by observation that in going from the 89-term to the 105-term $^1S$ wave function, $\alpha_{VP}$ changes only in the fourth decimal place, while $\epsilon$ changes considerally. Thus further improvement in the already highly accurate $^1S$ wave function (containing ~99.9% of the correlation energy) would make $\alpha-$ approach $\alpha_{VP}$ but would not significantly change the value of $\alpha_{VP}$. There is, of course, the possibility that a more accurate $^1P$ wave function could change $\alpha-$ and

TABLE II. Comparison of our polarizability results for four-electron atoms and ions with other calculations. Values reported are in cubic angstroms ($\text{Å}^3$). Our results in $a_0^3$ were converted to $\text{Å}^3$ by use of $1a_0 = 0.529167$ Å.

| Method | Ref. | Be I | C III | O v |
|---|---|---|---|---|
| Uncoupled Hartree-Fock (UCHF) | 10 | 9.54 | 0.653 | |
| Approximate UCHF (AUCHF) | 11 | 7.77 | | |
| Distinguishable-electron method | 12 | 7.55 | 0.565 | |
| Coupled Hartree–Fock (CHF) | 13 | 6.99 | 0.802 | |
| Brueckner–Goldstone perturbation | 14, 15 | 6.93 | | |
| CHF | 16, 17 | 6.76 | 0.67 | |
| Coupled perturbed Hartree–Fock (CPHF) | 18 | 6.733 | | |
| Perturbed uncoupled HF (PUCHF) and geometric extension (GPUHF) | 19 | 6.672 | | |
| Unrestricted HF | 20 | 6.24 | 0.497 | |
| CPHF (estimate) | 18 | 6.15 | | |
| GPUHF | 21 | 6.07 | | |
| PUCHF | 20 | 5.54 | 0.398 | |
| Perturbation-variation | 22 | 5.49 ± 0.5 | | |
| Multiconfiguration SCF | 23 | 5.41 ± 0.25 | | |
| Present results | | 5.42 ± 0.12 | 0.5401 | 0.1526 |
| Rigorous lower bounds (present calculation) | | 5.297 | 0.5175 | 0.1462 |
| Oscillator strength sums | 24 | 5.36 < α < 6.62 | | |
| AUCHF | 25 | 4.54 | | |
| AUCHF | 26 | 4.53 | | |
| CHF | 27 | 4.5 | | |
| UCHF | 28 | 4.28 | 0.398 | |
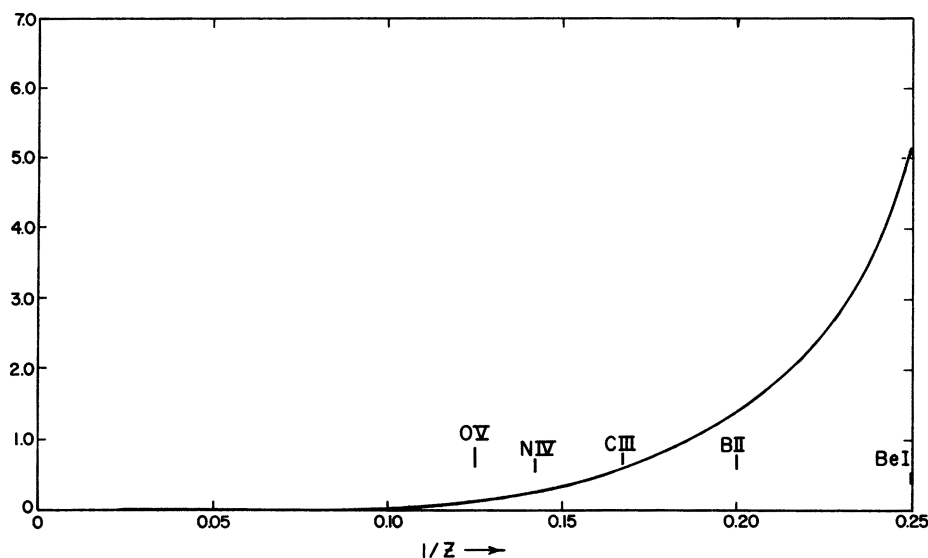
FIG. 1. Polarizabilities (in Å³) for the Be isoelectronic sequence (¹S ground states).

$\alpha_{VP}$, but the $^1P$ wave function is already of con-
siderable accuracy ($E = -14.472\,46$ a.u. versus an
estimated exact nonrelativistic energy of
$-14.472\,67$ a.u.[6]), and $E^{(2)}$ and thus $\alpha$ are known to
be relatively insensitive to the correction $\varphi^{(1)}$.[4]

In Table II we present a comprehensive compari-
son of the present results with various previous
theoretical values. The values which are under-
lined are ruled out by our rigorous bounds. The
rest of the values fall above our rigorous bounds
and cannot be ruled out. However, the rate of
convergence of our calculations tends to support
the perturbation-variation results of Kolker and
Michels[22] and the multiconfiguration self-consis-
tent field (MCSCF) results of Stevens and Billings-
ley.[23] By far the most extensive calculation to
date of the polarizability of Be I is the calculation
of Stevens and Billingsley. Our results are con-
sistent with theirs. In view of the fact that our
wave functions treat correlation more extensively
than theirs, and are the most extensive variation-
perturbation results to date, we recommend the
value of 5.42 Å³ for the polarizability, with an
estimated accuracy of ≤2%. For C III and O V, the
energies of $\varphi^{(0)}$ and $\varphi^{(1)}$ were not as exhaustively
minimized, so that an accuracy of ≤5% should
probably be assigned to these values.

### A. Polarizabilities of Higher Numbers of the Isoelectronic sequence

We have calculated lower bounds and variation-
perturbation estimates of the polarizability for
the berylliumlike ions $Z = 4$, 6, 8. To extend these
results to higher members of the sequence one can

resort to a general expression of $\alpha$ as a function
of nuclear charge $Z$ which arises in the $Z^{-1}$ pertur-
bation theory, and suggests that $Z^{-1}$ is the natural
parameter against which to plot $\alpha$ values in a
graphical display to the isoelectronic sequence.
The curve fitting our data and the knowledge that
$\alpha \to 0$ as $Z^{-1} \to 0$ [$\alpha(1\,^1S)$ can be expressed as func-
tion of $Z$ as

$$\alpha(1\,^1S) = C_4/Z^4 + C_5/Z^5 + \cdots]$$

is presented as Fig. 1, from which values of $\alpha$ (in Å³)
can be estimated for other $Z$ values.

### IV. CONCLUSIONS

On the basis of the results presented here, it
seems reasonable to conclude that the introduction
of $r_{ij}$ coordinates for an atomic wave function with
$N>3$ can lead to reliable polarizability values
(~2% accuracy). It also appears that to obtain re-
liable lower bounds to polarizabilities, wave func-
tions of considerable accuracy must be employed.
Recommended values for the polarizabilities of
the $^1S$ ground state have been presented for the
entire Be isoelectronic sequence.

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