

Self-Consistent Perturbation. II. Calculation of Quadrupole Polarizability and Shielding Factor

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Quadrupole polarizability and shielding factors for 2- and 4-electron closed-shell ions have been computed following the self-consistent-perturbation method. The results are accurate up to first order in the wave functions under the fully coupled Hartree-Fock approximation. The importance of choosing proper representation for perturbed orbitals is discussed.

I. INTRODUCTION

SINCE the first systematic working out of the theory of quadrupole polarizability and the property of antishielding of atoms and molecules by Sternheimer *et al.*,¹ many papers have appeared on the theoretical estimation of these parameters. In general, it has been looked upon as a perturbation problem with a Hamiltonian of the type $r^2(3 \cos^2\theta - 1)$. The methods of solution have been basically on the following lines. Sternheimer² writes down the first-order perturbation equation and solves it numerically. Das *et al.*³ and others⁴ treat it variationally and obtain the perturbed wave functions by minimizing the second-order energy. In all these calculations each orbital has been dealt with individually without any regard to the coupling that exists amongst them.

Dalgarno,^{5,6} Kaneko,⁷ and Allen⁸ have independently worked out the expression for the second-order energy under the fully coupled approximation. This when minimized, maintaining proper self-consistency, should yield the perturbed wave functions correctly. Khubchandani *et al.*⁹ started with Dalgarno's energy expression in their variational calculation, but subsequently did not retain the coupling among the perturbed orbitals. The complete Hartree-Fock (HF) equation including the perturbing potential has been solved by Watson and Freeman¹⁰ using the unrestricted Hartree-Fock (UHF) method.

In an earlier paper,¹¹ we have described a very convenient variation method for minimizing the second-

order energy under the fully coupled HF approximation, maintaining complete self-consistency. It incorporates all the features of a coupled HF calculation but is much simpler to handle. In order to consider the external field effect only, such a perturbation method is more advisable than a complete HF calculation because, to take care of the influence of a small part in the Hamiltonian up to a desired degree of accuracy, an HF calculation has to be carried out to a much higher precision; otherwise the effect is liable to be lost. In a perturbation approach on the other hand, the change due to the small Hamiltonian itself is directly calculated and there is very little chance of making such an error.

In the following section, the method described in I has been sketched in brief. The quadrupole polarizability and shielding factors have been defined in Sec. III. The results for the He and Be isoelectronic sequences are listed in Tables I and II. The perturbed wave function is used as a criterion for the correctness of calculation. Because of the unavailability of proper unperturbed UHF functions for the Li sequence, the results for these ions have not been quoted here. It has been observed that for accurate calculation of the present nature, the use of a restricted HF unperturbed function for an open-shell ion leads to appreciable inaccuracy in the final results.¹²

TABLE I. α_q and γ_∞ for the helium sequence with Roothaan best SCF unperturbed^a and 12-parameter perturbed functions.

Ion	α_q (10^{-40} cm ⁵)		γ_∞	
	This paper	Others	This paper	Others
He	0.09651	0.0965 ^b	0.396	0.397 ^b
Li ⁺	0.004648	0.00464 ^b	0.248	0.249 ^b
Be ²⁺	0.0006304		0.181	0.181 ^b
B ³⁺	0.0001415		0.142	0.142 ^b
C ⁴⁺	0.00004283		0.117	
N ⁵⁺	0.00001583		0.0996	
O ⁶⁺	0.000006742		0.0869	
F ⁷⁺	0.000003194		0.0767	
Ne ⁸⁺	0.000001644		0.0689	

^a See Ref. 13.

^b See Ref. 6.

¹² A comparison of the results in Table II (for the Li sequence) of Ref. 11 with those in Tables I and III (for the He and Be sequences) shows that the agreement of the computed values of β_∞ to N/Z is much less satisfactory in Table II than in Tables I and III.

¹ R. M. Sternheimer and H. M. Foley, *Phys. Rev.* **92**, 1460 (1953); H. M. Foley, R. M. Sternheimer, and D. Tycko, *ibid.* **93**, 734 (1954).

² R. M. Sternheimer, *Phys. Rev.* **96**, 951 (1954); **130**, 1423 (1963).

³ T. P. Das and R. Bersohn, *Phys. Rev.* **102**, 360 (1956); E. G. Wikner and T. P. Das, *ibid.* **107**, 497 (1958); **109**, 360 (1958).

⁴ G. Burns, *Phys. Rev.* **115**, 357 (1959); *J. Chem. Phys.* **31**, 1253 (1959); G. Burns and E. G. Wikner, *Phys. Rev.* **121**, 155 (1961); R. Ingalls, *ibid.* **128**, 1155 (1962).

⁵ A. Dalgarno, *Proc. Roy. Soc. (London)* **A251**, 282 (1959).

⁶ A. Dalgarno, *Advan. Phys.* **11**, 281 (1962).

⁷ S. Kaneko, *J. Phys. Soc. Japan* **14**, 1600 (1959).

⁸ L. C. Allen, *Phys. Rev.* **118**, 167 (1960).

⁹ P. G. Khubchandani, R. R. Sharma, and T. P. Das, *Phys. Rev.* **126**, 594 (1962).

¹⁰ R. E. Watson and A. J. Freeman, *Phys. Rev.* **131**, 250, 2566 (1963); **132**, 706 (1963); **135**, A1209 (1964).

¹¹ J. Lahiri and A. Mukherji (to be published), hereafter referred to as I.

II. THEORY

The theory of self-consistent perturbation method has been dealt with in detail in I. The essential features are summarized below for easy reference.

Let

$$H_0 = \sum_i s(i) + \sum'_{i,j} t(i,j) \quad (1)$$

represent the total unperturbed Hamiltonian for the system in the HF scheme, where $s(i)$ is the total one-particle interaction for the electron i and $t(i,j)$ is the Coulomb repulsion between the electrons i and j . Let

$$H_1 = \sum_i h_1(i) \quad (2)$$

represent the perturbing Hamiltonian which is assumed to be of single-particle nature. It can now be shown that the second-order energy expression for the system becomes

$$E_2 = \sum_k [I(\delta k, \delta k) + W(k, \delta k) + W(\delta k, k) - S(\delta k, \delta k) \epsilon_k] \\ + \sum_k \sum_{l(\neq k)} [J(\delta k, k | \delta l, l) + J(\delta k, k | l, \delta l) \\ + J(\delta k, \delta k | l, l) - J(\delta k, l | \delta l, k) - J(\delta k, l | l, \delta k) \\ - J(\delta k, \delta l | l, k)], \quad (3)$$

where

$$\epsilon_k = I(k, k) + \sum_{l(\neq k)} [J(k, k | l, l) - J(k, l | l, k)] \quad (4)$$

is the energy for the k th orbital. The other notation is as follows:

$$W(\delta a, b) = \int \delta \psi_a^*(i) h_1(i) \psi_b(i) d\tau_i,$$

$$I(\delta a, \delta b) = \int \delta \psi_a^*(i) s(i) \delta \psi_b(i) d\tau_i,$$

$$J(\delta a, b | c, \delta d) = \int \delta \psi_a^*(i) \psi_b(i) t(i, j) \psi_c^*(j) \delta \psi_d(j) d\tau_i d\tau_j,$$

and

$$S(\delta a, \delta a) = \int \delta \psi_a^*(i) \delta \psi_a(i) d\tau_i. \quad (5)$$

Here the ψ 's represent the one-electron unperturbed orbitals in the HF scheme and the $\delta\psi$'s are first-order changes to these orbitals due to the perturbing Hamiltonian H_1 . Each suffix or index a, b, k, l , etc., stands for the complete set of quantum numbers necessary to specify an unperturbed orbital uniquely, while $\delta a, \delta b$, etc., represent the same for perturbed orbitals.

In arriving at the expression (3) the following simplifying relations have been used:

$$I(\delta k, k) + \sum_{l(\neq k)} [J(\delta k, k | l, l) - J(\delta k, l | l, k)] \\ = \epsilon_k \langle \delta k | k \rangle = 0. \quad (6)$$

The orthonormality conditions up to the first order are maintained through

$$\langle \delta \psi_k | \psi_k \rangle = 0,$$

and

$$\langle \delta \psi_k | \psi_l \rangle + \langle \psi_k | \delta \psi_l \rangle = 0. \quad (7)$$

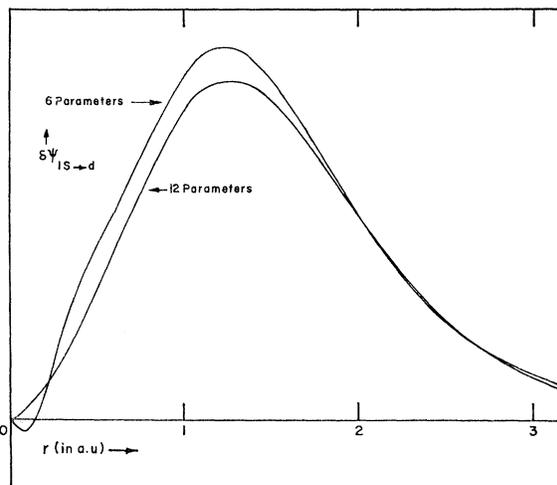


FIG. 1. Perturbed 1s orbital of Be atom for 6- and 12-parameter representations (a.u. = atomic units).

The $\delta\psi$'s are now determined by minimizing E_2 subject to Eqs. (7). Instead of handling the whole energy matrix in one block, a very convenient approach in which the parameters of only one orbital are considered at a time, has been described in I. Complete self-consistency maintaining the coupling among the perturbed orbitals can be achieved within a few iterations.

Regarding the choice of the form of $\delta\psi_k$'s, the angular and spin functions are taken to be of the same nature as appearing in $h_1\psi_k$ and a general and flexible form for the radial part is chosen as follows

$$\delta \psi_k(r_i) = \sum_a^{1,\mu} C_{kq} r_i^{nkq} \exp(-\zeta_{kq} r_i), \quad (8)$$

where C_{kq} 's are the variation parameters. Such a choice has proved successful and adequate while calculating the dipole polarizabilities and shielding factors for a number of ions listed in I.

TABLE II. α_q and γ_∞ for the beryllium sequence with Roothaan best SCF unperturbed^a and 12-parameter perturbed functions.

Ion	α_q (10^{-40} cm ⁵)		γ_∞	
	This paper	Others	This paper	Others
Be	14.21	14.2 ^b	0.786	{0.72 ^c 0.77 ^b }
B ⁺	1.173	1.17 ^b	0.549	{0.53 ^c 0.55 ^b }
C ²⁺	0.2168	0.22 ^b	0.428	0.43 ^b
N ³⁺	0.05945		0.351	
O ⁴⁺	0.02073		0.298	
F ⁵⁺	0.008496		0.259	
Ne ⁶⁺	0.003925		0.229	

^a See Ref. 13.

^b A. Dalgarno and H. A. J. McIntyre, Proc. Phys. Soc. (London) **85**, 47 (1965).

^c See Ref. 6.

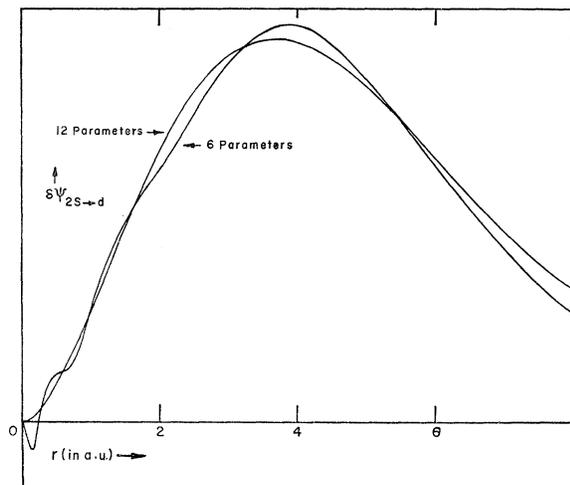


FIG. 2. Perturbed 2s orbital of Be atom for 6- and 12-parameter representations.

III. QUADRUPOLE POLARIZABILITY AND SHIELDING FACTOR

We shall consider here the effect on an atom or ion when placed in a nonuniform electric field. If the quadrupole moment induced in the electron cloud due to a gradient q of the electric field be Q , then the quadrupole polarizability for the system can be expressed as $\alpha_q = Q/q$. This induced moment Q will have its own contribution to the total field gradient at the nuclear site, which may be given by $\gamma_\infty q$ in a direction opposing q , where γ_∞ is the quadrupole shielding factor.

If q is assumed to be produced by a point charge Z' placed at a distance R from the nucleus along the z axis, and if R is sufficiently large compared to atomic dimensions, then the interaction potential of the electron system with q is⁶

$$V(r) = -Z' \sum_i (r_i^2/R^3) P_2(\cos\theta_i), \quad (9)$$

where $P_2(\cos\theta_i)$ is the Legendre polynomial of order

TABLE III. Comparison of computed quantities for Be atom with 6- and 12-parameter representations of the perturbed orbitals ($Z'=1.0$, $R=20$ atomic units).

No. of parameters	Second-order orbital energy (in a.u.)		α_q (in 10^{-40} cm ⁶)	γ_∞
	1s	2s		
6	-7.76×10^{-12}	-2.55×10^{-6}	13.5	1.40
12	-6.91×10^{-12}	-2.68×10^{-6}	14.2	0.79
Discrepancy	12%	5%	5%	77%

two. The quadrupole polarizability is then given by

$$\alpha_q = \frac{2R^3}{Z'} \int_0^\infty \Psi_1 \sum_i r_i^2 P_2(\cos\theta_i) \Psi_0 d\tau_i, \quad (10)$$

and the quadrupole shielding factor is

$$\gamma_\infty = \frac{2R^3}{Z'} \int_0^\infty \Psi_1 \sum_i \frac{P_2(\cos\theta_i)}{r_i^3} \Psi_0 d\tau_i. \quad (11)$$

It may be mentioned that a factor of $\frac{1}{2}$ has been omitted in the above expression for α_q in order to keep it in conformity with the usual convention first introduced by Sternheimer.²

The calculations have been carried out in the cases of 2- and 4-electron closed-shell ions with the "best SCF" wave functions of Roothaan, Sachs, and Weiss.¹³ The results are listed in Tables I and II. The values obtained by other coupled HF calculations of comparable accuracy, wherever available, have also been quoted. Our computations were performed on the CDC 3600 electronic computer at Tata Institute of Fundamental Research, Bombay.

In the case of dipole polarizability calculation, the computed values of the shielding factor provide an absolute check on the accuracy. For quadrupole polarizability calculations, however, no such test is available. The study of the perturbed orbitals offers a good indication as to the adequacy of the analytic form chosen to represent it. In Figs. 1 and 2, we have plotted the perturbed 1s and 2s wave functions for the Be atom with 6 and 12 variation parameters. The 6-parameter functions are evidently inadequate. The small loops near the origin strongly influence the value of γ_∞ , while α_q and the perturbed energies are comparatively less affected. This is illustrated in Table III. The slow convergence of the computed value of γ_∞ , as has been observed by many workers,¹⁴ is thus solely due to the fact that the perturbing potential (9) weights the region away from the nucleus, whereas the value of γ_∞ is principally determined by the behavior of the wave function near the origin. Energy convergence is not a good test to guarantee a proper description of the orbitals in this region. The perturbed function should be studied graphically to ensure that it has attained a stable shape.

¹³ C. C. J. Roothaan, R. A. Sachs, and A. W. Weiss, *Rev. Mod. Phys.* **32**, 186 (1960).

¹⁴ See, for example, A. Dalgarno, W. D. Davison, and A. L. Stewart, *Proc. Roy. Soc. (London)* **A257**, 115 (1960).