

Effect of a crystalline spherical potential on the Fermi-contact term in Mn^{2+} and Fe^{3+} ions

K. D. Sen*

*Institut für Physikalische Chemie, Physikalische Chemie III,
Technische Hochschule Darmstadt, 6100 Darmstadt, West Germany
(Received 20 February 1979)*

The Watson-sphere model (WSM) has been applied to obtain the crystal-ion Fermi-contact parameter χ for Mn^{2+} and Fe^{3+} within Gopinathan's approximate unrestricted Hartree-Fock procedure. A comparison with the free-ion calculations shows that whereas the shell-wise contributions to χ are significantly altered, the total χ in the WSM remains the same as for the free ions.

I. INTRODUCTION

The core-polarization effects¹ in atoms and ions are associated with the spin-dependent exchange interaction between the core and the unpaired valence electrons. The recently developed experimental methods of Mössbauer conversion electron spectroscopy² and x-ray photoemission spectroscopy³ are capable of directly measuring the contact densities χ_{nl} defined as the net spin density (of the n /th shell) at the nucleus. Our understanding of such experimental data for the ionic solids of $3d$ transition-metal ions is mostly based on the nonrelativistic unrestricted Hartree-Fock (UHF) calculations⁴ on the free ions. Recent calculations of χ_{nl} incorporating the relativistic⁵ and correlation⁶ effects on the related systems suggest that such effects are expected to be small for the positive ions such as Mn^{2+} and Fe^{3+} . A few cluster model calculations have been reported⁷ which account for the covalency effects. Although the UHF calculations for the free ions Mn^{2+} and Fe^{3+} provide a fairly good description of the total contact density χ , there is experimental evidence⁸ that indicates that the total radial charge density of the positive ions in ionic crystals undergoes a net expansion relative to the free ion. It is of interest to study the influence of such expansions on the χ_{nl} by means of a simple model which simulates this particular crystal-ion behavior. The Watson-sphere model⁹ (WSM) for ions in crystals has been extensively used to study (to zeroth order) the influence of crystalline electrostatic effects on properties such as the diamagnetic susceptibility, dipole and quadrupole polarizabilities, and Sternheimer shielding-antishielding factors,¹⁰ and it has been observed that these results differ significantly from the free-ion values and are always in better agreement with the experimental estimates of the property in question. In this paper we report the results of our calculations of χ for Mn^{2+} and Fe^{3+} ions which used the WSM within an approximate numerical UHF

scheme. These results are then compared with the free-ion calculations to study the variation of χ_{nl} and χ in the two cases.

In Sec. II we give a brief account of the method of calculation adopted here. In Sec. III we present our results and derive conclusions from them.

II. METHOD OF CALCULATIONS

The approximate UHF scheme adopted by us uses an improved representation¹¹ of the Slater exchange approximation¹² recently suggested and tested successfully on the $3d$ ions. The method yields χ_{nl} values in excellent agreement with the UHF calculations wherein no such exchange approximation is invoked. The improvement over the conventional Slater exchange approximation¹³ is obtained by treating the self-interaction potential accurately and analyzing the properties of the Fermi hole for the true HF exchange potential. One starts with the one-electron HF equations (in Rydberg units) as

$$[f_i + V_C(r) + V_s + V_{ex}]u_i(r) = \epsilon_i u_i(r), \quad (1)$$

where the u_i 's are the spin orbitals with occupancy n_i ; $f_i = -\nabla^2 - 2Z/r$; V_C , V_s and V_{ex} , respectively, denote the Coulomb potential, self-interaction, and the true HF exchange potential for the i th electron given by

$$V_C(r) = \sum_j n_j \int u_j^*(r) u_j(r') g_{rr'} dr', \quad (2)$$

$$V_s(r) = -n_i \int u_i^*(r') u_i(r') g_{rr'} dr', \quad (3)$$

and

$$V_{ex}(r) = - \sum_{j \neq i} \frac{n_j \int u_i^*(r) u_j^*(r') u_j(r) u_i(r) g_{rr'} dr'}{u_i^*(r) u_i(r)}. \quad (4)$$

Using the characteristic properties of the Fermi sphere and assuming that the exchange charge densi-

ty varies linearly over it according to

$$\rho_i^{\text{ex}}(r) = ar + b, \quad (5)$$

with the appropriate boundary conditions

$$\rho_i^{\text{ex}}(r=0) = -\rho_i(1)$$

and

$$\rho_i^{\text{ex}}(r=r_0) = -\rho_i(1)/n_i,$$

Gopinathan¹⁰ has derived that

$$V_{\text{ex}}(r) = -g \frac{\alpha}{2} \left(2\rho_i'(r) \rho^{-2/3}(r) - \frac{2}{3} \rho^{-5/3}(r) \right) \times \sum_{\text{spin}} n_i u_i(r) u_i(r) \rho_i(r), \quad (6)$$

with

$$\alpha = \frac{8}{(2\pi)^{2/3}} \left(\frac{1}{n} + \frac{1}{2} \right) \left/ \left(\frac{1}{n} + \frac{1}{3} \right) \right|^{2/3}, \quad (7)$$

where n gives the number of electrons with a particular spin. ρ_i' gives the total charge density of the like spin ρ_i less the i th-electron density. We have used the average value of α as 0.7319 in our calculations. Equation (1) has the correct asymptotic behavior as $r \rightarrow \infty$ so that no unphysical tail corrections have to be employed. From the point of view of calculating χ , Eq. (1) provides as good approximation to the HF potential, particularly for the inner shells near the nucleus since the self-interaction term makes the dominant contribution to the exchange potential in this region.

In the WSM the electrostatic potential acting on the crystal ion A^{+q} is simulated by superimposing the electrostatic potential of a uniformly charged hollow sphere carrying a total charge of $-q$ units. The ion A^{+q} is assumed to be situated at the center of the sphere and the sphere radius is chosen as Pauling's

ionic radius, r_{ion} . The crystal-ion wave functions are then generated self-consistently with the addition of the Watson-sphere potential V_W to Eq. (1)

$$V_W = \begin{cases} \frac{2qe}{r_{\text{ion}}}, & \text{for } r_i \leq r_{\text{ion}}, \\ \frac{2qe}{r_i}, & \text{for } r_i \geq r_{\text{ion}}. \end{cases} \quad (8)$$

The quantity is defined (in a.u.) as

$$\chi = \frac{4\pi}{n_1 - n_l} \sum_n \rho_{ns}^1(0) - \rho_{ns}^1(0) = \sum_n \chi_{ns}, \quad (9)$$

where $\chi_{ns}(0)$ give the electron density (at the nucleus) contributed by spin orbitals ns . By convention, the majority spin has been taken as spin-up. The $\rho_{ns}(0)$ are obtained from an expansion of the wave functions near the nucleus in appropriate polynomials followed by extrapolation to $r=0$. The calculations have been carried out using a modified Herman-Skillman program¹⁴ in double-precision arithmetic on the IBM 370/168 system at the Technische Hochschule Darmstadt. We have used a 441-point radial mesh and have demanded that the χ_{ns} be self-consistent to within 0.01 a.u. Computationally, the present calculations are as simple as the earlier unrestricted Hartree-Fock-Slater (HFS) calculations.¹²

II. RESULTS AND CONCLUSIONS

A comparison of the free- and crystal-ion calculations shows identical trends in the cases of Mn^{2+} and Fe^{3+} and in the following discussion we shall treat them together.

Table I contains the one-electron eigenvalues ϵ_i

TABLE I. Comparison of free-ion and crystal-ion eigenvalues $-\epsilon_i$, for Mn^{2+} and Fe^{3+} by HF and the present model (Ref. 11). The HF values are taken from Refs. 13 and 15, respectively. The free-ion HF values of $-\epsilon_i$ for Fe^{3+} pertain to the restricted HF calculations in Ref. 15. The crystal-ion $-\epsilon_i$ values correspond to use of a Watson sphere with radius equal to the Pauling ionic radius. ϵ_i values in Ry units.

Orbital	Mn^{2+} (Present)	Free-ions			Crystal-ions	
		Mn^{2+} (HF)	Fe^{3+} (Present)	Fe^{3+} (HF)	Mn^{2+}	Fe^{3+}
1s ↑	480.72	482.37	523.91		478.63	520.29
1s ↓	480.73	482.37	523.93	525.53	478.64	520.30
2s ↑	59.36	59.66	66.64		57.27	62.97
2s ↓	59.06	59.63	66.28	66.67	56.99	62.66
3s ↑	8.99	9.32	11.20		6.77	7.13
3s ↓	8.31	8.49	10.45	11.04	6.13	6.47
2p ↑	52.31	51.04	59.19		50.22	55.53
2p ↓	52.11	50.78	58.95	57.63	50.04	55.34
3p ↑	6.75	6.75	8.77		4.53	4.71
3p ↓	6.08	5.75	8.04	8.17	3.90	4.07
3d ↑	3.10	2.58	4.76	4.15	0.87	0.73

TABLE II. Fermi-contact term [Eq. (9)] χ for Mn^{2+} and Fe^{3+} in free- and crystal-ion cases, respectively. Free-ion HF values have been taken from Ref. 4 for comparison with the present values. The crystal-ion values correspond to use of Watson-sphere radii of 0.64 and 0.84 Å for Mn^{2+} and Fe^{3+} , respectively. All values are given in a.u.

Orbital	Mn^{2+} (Present)	Free ions		Fe^{3+} (HF)	Crystal-ions	
		Mn^{2+} (HF)	Fe^{3+} (Present)		Mn^{2+}	Fe^{3+}
1s	-0.08	-0.19	-0.19	-0.25	-0.10	-0.14
2s	-7.72	-7.15	-9.37	-8.51	-7.23	-7.99
3s	+3.41	+3.22	+4.76	+5.77	+2.94	+3.46
	-4.39	-4.13	-4.81	-3.0	-4.39	-4.67

[Eq. (1)] along with the corresponding free-ion HF values. Although the presently calculated ϵ_i should not be directly compared with the HF values, as already noted earlier, due to the similar exact treatment of the self-interaction term, the two free-ion ϵ_i values are in close agreement with each other. No calculations of ϵ_i corresponding to the WSM in UHF approximation are available. In the presence of the WS, the ϵ_i values are found to have risen above their free-ion counterparts; this indicates an associated net expansion of the charge density. Such effects have been more directly demonstrated earlier⁹ by plotting the radial charge density corresponding to the free and crystal ion within the WS model, respectively. As expected, the total percentage effect is largest for the loosely bound 3d electrons.

The result of the earlier UHF calculations of χ for the free ions of the 3d series can be summarized as follows. The 1s and 2s orbitals make a negative contribution (denoted by χ_{1s} and χ_{2s} , respectively) to χ which suggests that these orbitals could be treated as internal to the core-polarizing d orbital. The 3s orbital contribution, χ_{3s} , is positive, i.e., it behaves as if it were external to the 3d orbital. The magnitude of χ_{1s} is very small. The net χ is a result of large cancellations between χ_{2s} and χ_{3s} and is negative since $|\chi_{2s}| > |\chi_{3s}|$.

In Table II we give the χ_{ns} values for Mn^{2+} and Fe^{3+} ions calculated in the present work as well as the results of the earlier UHF calculations. The two free-ion calculations are found to be in good agreement with each other. The general trends of the free-ion χ_{ns} values are maintained in the present

crystal-ion calculations. Due to the weak 1s-3d exchange interaction, χ_{1s} remains almost constant in going from free- to the crystal-ion state within the present model. Both the 2s and 3s electrons lose considerable amounts of exchange interaction but the magnitude of the changes with the respective χ_{nl} are nearly equal. As a result, for the total χ for the value of the radius of the WS equal to the Pauling ionic radius, 0.84 and 0.64, respectively, we obtain $\chi(\text{Mn}^{2+}) = 4.39$ and $\chi(\text{Fe}^{3+}) = 4.67$ a.u. compared to the free-ion values of 4.39 and 4.81 a.u., respectively.

In conclusion, the present calculations show that although the 2s and 3s orbital contributions to χ diminish in magnitude in going from free- to the crystal-ion state, the total value of χ remains almost unchanged. As a result, the good agreement obtained earlier between the free-ion estimates of χ and the corresponding experimental values remains unchanged. It would be instructive to perform a relativistic many-body perturbation theoretical calculation starting with the WSM as the zeroth order. In the cases of negative ions such as O^- , even at the zeroth order one expects significant changes in χ (due to the Watson sphere) over the free-ion results; such calculations are underway at present.

ACKNOWLEDGMENTS

It is a pleasure thanks to Professor Alarich Weiss, for his interest in this work. The author is grateful to the Alexander von Humboldt Foundation for the award of the Junior Research Fellowship under which this work has been carried out.

[†]On leave from School of Chem., Univ. of Hyderabad, India.

¹R. M. Sternheimer, Phys. Rev. **86**, 316 (1952); A. Abragam, J. Horowitz, and M. H. L. Pryce, Proc. R. Soc. London Ser. A **230**, 169 (1955).

²C. J. Song, J. Trooster, and N. Benczer-Köller, Phys. Rev. B **9**, 3854 (1974).

³S. Hüfner and G. K. Wertheim, Phys. Rev. B **7**, 2333 (1973).

⁴A. J. Freeman and R. E. Watson, *Magnetism*, edited by G.

- Rado and H. Suhl (Academic, New York, 1965), Vol. II A. See also, P. S. Bagus, B. Liu, and H. F. Schaefer III, Phys. Rev. A 2, 555 (1970) for more recent work.
- ⁵J. P. Desclaux, A. J. Freeman, and J. V. Mallow, J. Magn. Mater. 5, 265 (1977); J. P. Desclaux and A. J. Freeman, *ibid.* 8, 119 (1978); A. J. Freeman, Phys. Scr. 15, 80 (1977) for a recent review.
- ⁶J. Andriessen, M. Vajed-Samii, K. Raghunathan, S. N. Ray, and T. P. Das, Hyperfine Interact. 4, 91 (1978); Phys. Rev. B 15, 2533 (1977).
- ⁷E. Byrom, A. J. Freeman, and D. E. Ellis, in *Proceedings of the 20th Conference on Magnetism and Magnetic Materials, 1974*, edited by C. D. Graham, Jr., G. H. Lander, and J. J. Rhyne, AIP Conf. Proc. No. 24 (AIP, New York, 1975), p. 209; Phys. Rev. B 14, 3558 (1976).
- ⁸M. P. Tosi, Solid State Phys. 16, 1 (1964).
- ⁹R. E. Watson, Phys. Rev. 124, 1283 (1961).
- ¹⁰E. Paschalis and A. Weiss, Theor. Chim. Acta 7, 189 (1967); K. D. Sen and P. T. Narasimhan, Phys. Rev. B 15, 95 (1977); P. C. Schmidt, A. Weiss, and T. P. Das, Phys. Rev. B 19, 5525 (1979).
- ¹¹M. S. Gopinathan, Phys. Rev. A 15, 2135 (1977).
- ¹²J. C. Slater, Phys. Rev. 81, 385 (1951).
- ¹³T. H. Wilson, J. H. Wood, and J. C. Slater, Phys. Rev. A 2, 620 (1970).
- ¹⁴F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, 1963).
- ¹⁵E. Clementi and C. Roetti, At. Data Nucl. Data Tables, 14, 177 (1974).