A comparison of ZnO and ZnO^-

Charles W. Bauschlicher, Jr. and Harry Partridge

NASA Ames Research Center

Moffett Field, CA 94035

Abstract

Ab initio electronic structure calculations are performed to support and to help interpret the experimental work reported in the proceeding manuscript. The CCSD(T) approach, in conjunction with a large basis set, is used to compute spectroscopic constants for the $X^1\Sigma^+$ and $^3\Pi$ states of ZnO and the $X^2\Sigma^+$ state of ZnO^-. The spectroscopic constants, including the electron affinity, are in good agreement with experiment. The ZnO EA is significantly larger than that of O, thus relative to the atomic ground state asymptotes, ZnO^- has a larger D_0 than the $^1\Sigma^+$ state, despite the fact that the extra electron goes into an antibonding orbital. The changes in spectroscopic constants can be understood in terms of the $X^1\Sigma^+$ formally dissociating to Zn ^1S + O ^1D, while the $^3\Pi$ and $^2\Sigma^+$ states dissociate to Zn ^1S + O ^3P and Zn ^1S and O^- ^2P, respectively.

I. INTRODUCTION

Fancher, de Clercq, Thomas, and Bowen[1] recently measured the photoelectron detachment spectra of ZnO^-. Their electron affinity (EA) of ZnO is 2.088±0.010 eV, which is significantly larger than that of O (1.461 eV[2]). This means that the D_0 of ZnO^- is 0.63 eV larger than that of ZnO (1.61±0.04 eV[3]), if both are computed

with respect to the atomic ground states. While the D_0 was larger, the r_e of ZnO^- is 0.07 Å longer than that of the neutral. Consistent with the longer bond length, their ZnO^- ω_e value (625 cm^{-1}) is smaller than that for the neutral[4] (811 cm^{-1}). The spectra also exhibited some features that might indicate a very low-lying electronic state of ZnO.

Bauschlicher and Langhoff previously[5] studied ZnO and found the ground state to be $^1\Sigma^+$, however, the $^3\Pi$ state was extremely low-lying. The Zn $1s$-$3d$ and O $1s$ and $2s$ orbitals are not involved in the bonding, thus the valence occupation of these two states is $9\sigma^2 4\pi^4$ and $9\sigma^2 10\sigma^1 4\pi^3$, where the 9σ orbital is a bond between Zn $4s$ and O $2p\sigma$ orbitals, the 10σ orbital is the antibonding combination of the same orbitals, and the 4π orbital is mostly the O $2p\pi$ orbital with some donation to the Zn $4p\pi$ orbital. Given these occupations for the two lowest states of ZnO, the ground state of ZnO^- is $^2\Sigma^+$ with an occupation of $9\sigma^2 10\sigma^1 4\pi^4$. Thus relative to the ground $^1\Sigma^+$ state, ZnO^- has the additional electron in the 10σ antibonding orbital. Given the occupations of the ground states of ZnO and ZnO^- it appears strange that the D_0 of ZnO^- should be significantly larger than that of ZnO. While the relative D_0 values seem inconsistent with the occupations, the relative r_e and ω_e values show the expected trends.

In light of the unexpected results, we have performed accurate calculations for ZnO and ZnO^- to confirm the experimental observations and to understand the bonding. We also perform accurate calculations on both the $^1\Sigma^+$ and $^3\Pi$ states of ZnO to position these states and therefore help interpret the spectra. We also report results obtained using density functional theory (DFT), to compare the results of these inexpensive calculations with those obtained at the higher level of theory.

II. METHODS

The DFT calculation are performed using the hybrid[6] B3LYP functional[7] in conjunction with the 6-311+G(2d) basis set[8–11]. These calculations are performed using Gaussian 94[12]. The accurate calculations use the coupled cluster singles and doubles approach[13] including the effect of unlinked triples, which is determined using perturbation theory[14]; this approach is denoted CCSD(T). The restricted open-shell CCSD(T) approach[15,16] is used. In these calculations the O $1s$-like orbital and Zn $1s$-like to $3p$-like orbitals are not correlated. In the CCSD(T) calculations, the Zn basis sets is the $(20s\ 15p\ 9d\ 6f\ 4g)/[7s\ 6p\ 4d\ 3f\ 2g]$ atomic natural orbital[17] (ANO) set that has been described previously[18]. The O basis set is the augmented correlation-consistent polarized-valence quadruple zeta (aug-cc-pVQZ) set developed by Dunning and co-workers[19,20]. Only the spherical harmonic components of the basis sets are used. These CCSD(T) calculations are performed using MOLPRO 96[21].

In order to gain insight into the bonding, the modified coupled pair functional[22] (MCPF) natural orbitals are plotted. These calculations are performed at the B3LYP geometries. The basis set is that used in the B3LYP calculations with the diffuse Zn functions deleted and the two O $3d$ functions replaced by one with an exponent of 0.8. Using this basis set, self-consistent-field (SCF) based constrained space orbital variation[23] (CSOV) calculations are also performed. These MCPF and CSOV calculations were performed using the Molecule-Sweden program system[24].

III. RESULTS AND DISCUSSION

The results of our calculations are summarized in Table I along with the previous CPF results[5]. The present calculations use a much larger basis set and the CCSD(T) approach yields a much better description of the electron correlation than does the CPF, thus the current CCSD(T) results are much superior to the old CPF results.

For the $^1\Sigma^+$ state, which is not as well described by a single configuration as the $^3\Pi$ state, CCSD(T) yields a much larger D_0, a higher frequency, and a shorter bond length than the CPF. The computed D_0 value is in excellent agreement with the experimental value[3] of 1.61±0.04 eV. We expect our computed value to be too small by approximately 0.1 eV, therefore, we conclude that the experimental value is probably slightly too small. Unlike D_0, the computed ω_e value (727 cm^{-1}) is significantly smaller than the experimental value[4] of 811 cm^{-1}; a difference of this magnitude is unexpected. The CCSD(T) value is significantly better than the older CPF value. The $^3\Pi$ state, which is better described by a single reference, shows smaller changes with the improvements in the calculations, and as a result, the T_e value at the CCSD(T) level is much larger than reported previously. Thus while the old calculations suggest electron detachment should form two states at about the same energy, the current CCSD(T) results shows that the $^3\Pi$ state is about 0.26 eV above the $^1\Sigma^+$ state.

The computed change in r_e between ZnO^- and ZnO (0.045 Å) is smaller than found in experiment (0.07 Å). In addition, the computed ω_e of the $^2\Sigma^+$ state (664 cm^{-1} is only in reasonable agreement with experiment (625 cm^{-1}). Unlike the $X^1\Sigma^+$ state, the computed value is too large for the $^2\Sigma^+$ state. The norm of the singles amplitudes suggests that the $^2\Sigma^+$ state is the most difficult to describe, and therefore probably has a slightly larger error than the two neutral states. The computed EA is too small, as expected. However part of this error arises from the error in the EA of the O atom (1.403 vs 1.461 eV). If we shift the Zn+O and Zn+O^- asymptotes to agree with experiment, the corrected ZnO EA (2.03 eV) is in better agreement with experiment (2.088 eV). Thus the CCSD(T) calculations confirm the experimental observation that the EA of ZnO is significantly larger than that of O, that the ZnO^- r_e value is larger and the ω_e value is smaller than those found for the ground state of ZnO.

In Table I we also give results obtained at the B3LYP level. The r_e values are in reasonable agreement with the CCSD(T), in fact for the $^1\Sigma^+$ state the B3LYP results

agree better with the CCSD(T) than do the old CPF results. The accuracy of the ω_e values is mixed, for the $^1\Sigma^+$ state the agreement is very good, while for $^3\Pi$ and $^2\Sigma^+$ states the B3LYP results are about 70 cm^{-1} smaller than the CCSD(T). The D_0 values are too small and the B3LYP incorrectly places the $^3\Pi$ state below the $^1\Sigma^+$ state. The ZnO EA at the B3LYP level is too large, as is the EA of O atom. However, the corrected ZnO EA value agrees with experiment about as well as the CCSD(T) result. Overall the B3LYP results are reasonably accurate.

The MCPF valence natural orbitals for the $^3\Pi$ state of ZnO are plotted in Figs. 1, 2 and 3. The orbitals for the $^1\Sigma^+$ state of ZnO and for the $^2\Sigma^+$ state of ZnO^- are shown in Figs. 4-8. The MCPF populations are given in Table II. From the plots of the σ orbitals it is clear that the Zn undergoes $4s4p$ hybridization, and these form a bonding and antibonding orbital with the O $2p\sigma$ orbital. The 4π is mostly O $2p\pi$ with some donation to the Zn. The orbitals of ZnO^- are somewhat more diffuse than for the two states of ZnO. Thus the bonding is much as expected and there are no changes in the bonding between the three states considered in this work. A CSOV analysis at the self-consistent-field level shows only small changes in the importance of Zn to O donation, O to Zn donation and of the strength of the σ bond.

In the $^3\Pi$ state, there is single σ bond and the bonding is enhanced by O $2p\pi$ donation to Zn. In ZnO^-, the σ bonding still occurs but with an additional electron in the oxygen $2p\pi$ orbital, the polarization of the 9σ is much smaller, thus the σ bonding is more covalent and less ionic. The extra electron in the 4π orbital results in more O π donation to the Zn. Thus the bonding in ZnO^- is stronger than in the $^3\Pi$ state, and the relative D_0, r_e, and ω_e values are consistent with this.

The bonding in the $^1\Sigma^+$ state can be viewed as arising from Zn^+ $^2S(4s^1)$ + O^- $^2P(2p\sigma^1 2p\pi^4)$ or Zn ^1S + O $^1D(2p\sigma^0 2p\pi^4)$. The population suggest that the bonding is derived from about equal mixtures of these two asymptotes. In the ionic limit, a bond forms between the Zn $4s$ and O $2p\sigma$ orbitals and no promotion energy is

required to form hybrid orbitals. The O 2π donation is larger than for the $^3\Pi$ state since O^- should donate more electrons than O. In the $^1S+^1D$ limit, the Zn donates $4s$ electron density to the empty O $2p\sigma$ and the O $2p\pi$ orbital donates electrons to the Zn. The bonding is expected to be reasonably strong, and like the ionic asymptote no Zn hybridization is required. Thus the bonding in ZnO $^1\Sigma^+$, relative to these two asymptotes, is stronger than in ZnO^- relative to the $Zn+O^-$ asymptote. The D_0 of ZnO $^1\Sigma^+$ reported in this and previous work[3,5] is relative to Zn ^1S and O ^3P, buth this ignores the promotion energy to reach the asymptote to which the $^1\Sigma^+$ state formally dissociates. The O ^1D state is 1.97 eV above ^3P (note the Zn^++O^- asymptote is even higher at 7.93 eV above the ground state asymptote). Therefore if the bonding in ZnO $^1\Sigma^+$ is compared to its asymptote, the D_0 and ω_e decrease and r_e increases when ZnO^- is formed by adding an electron to an antibonding orbital.

IV. CONCLUSIONS

The computed CCSD(T) spectroscopic constants are in good agreement with experiment. The calculations show that the $^3\Pi$ state is not as low-lying as indicated by previous calculations. The ZnO EA is significantly larger than that of O, despite the extra electron going into an antibonding orbital. This is consistent with ZnO $^1\Sigma^+$ formally dissociating to Zn ^1S and O ^1D. Thus relative to the appropriate asymptote, the D_0 and ω_e of ZnO^- are smaller and the r_e longer than in the $X^1\Sigma^+$ state of ZnO, which is consistent with the electron going into an antibonding orbital. Relative to the $^3\Pi$ state, the additional electron increases the O to Zn π donation, and as a result, ZnO^- is more strongly bound, has a larger ω_e and shorter bond length than the $^3\Pi$ state of ZnO. The B3LYP results are in reasonable agreement with the CCSD(T), but important differences are observed.

REFERENCES

[1] C. A. Fancher, H. L. de Clercq, O. C. Thomas, and K. H. Bowen, the proceeding paper.

[2] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **14**, 731 (1985).

[3] D. E. Clemmer, N. F. Dalleska, and P. B. Armentrout, J. Chem. Phys. **95**, 7263 (1991).

[4] E. S. Prochaska and L. Andrews, J. Chem. Phys. **72**, 6782 (1980).

[5] C. W. Bauschlicher and S. R. Langhoff, Chem. Phys. Lett. **126**, 163 (1986).

[6] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[7] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, J. Phys. Chem. **98**, 11623 (1994).

[8] M. J. Frisch, J. A. Pople, and J. S. Binkley, J. Chem. Phys. **80** (1984) 3265 and references therein.

[9] A. J. H. Wachters, J. Chem. Phys. **52**, 1033 (1970).

[10] P. J. Hay, J. Chem. Phys. **66**, 4377 (1977).

[11] K. Raghavachari and G. W. Trucks, J. Chem. Phys. **91**, 1062 (1989).

[12] Gaussian 94, Revision D.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh

PA, 1995.

[13] R. J. Bartlett, Annu. Rev. Phys. Chem. **32**, 359 (1981).

[14] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).

[15] P. J. Knowles, C. Hampel, and H.-J. Werner, J. Chem. Phys. **99**, 5219 (1993).

[16] J. D. Watts, J. Gauss, and R. J. Bartlett, J. Chem. Phys. **98**, 8718 (1993).

[17] J. Almlöf and P. R. Taylor, J. Chem. Phys. **86**, 4070 (1987).

[18] C. W. Bauschlicher, M. Rosi, and S. R. Langhoff, Chem. Phys. **146**, 237 (1990).

[19] T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).

[20] R. A. Kendall, T. H. Dunning, and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).

[21] MOLPRO 96 is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer, A. J. Stone, and P. R. Taylor. The closed shell CCSD program is described in C. Hampel, K. Peterson, and H.-J. Werner, Chem. Phys. Lett. **190**, 1 (1992).

[22] D. P. Chong and S. R. Langhoff, J. Chem. Phys. **84**, 5606 (1986).

[23] P. S. Bagus, K. Hermann, and C. W. Bauschlicher, J. Chem. Phys. **80**, 4378 (1984).

[24] MOLECULE-SWEDEN is an electronic structure program written by J. Almlöf, C. W. Bauschlicher, M. R. A. Blomberg, D. P. Chong, A. Heiberg, S. R. Langhoff, P.-Å. Malmqvist, A. P. Rendell, B. O. Roos, P. E. M. Siegbahn, and P. R. Taylor.

TABLES

TABLE I. Summary of computed results.

Molecule	r_e(Å)	ω_e^a(cm^{-1})	$\omega_e\chi_e$(cm^{-1})	D_0(eV)	T_e(eV)	EA^b(eV)
CCSD(T)						
ZnO $^1\Sigma^+$	1.719	727.2	5.83	1.63		1.97(2.03)
ZnO $^3\Pi$	1.857	566.6	4.36	1.38	0.26	
ZnO$^-$ $^2\Sigma^+$	1.764	664.4	3.94	2.20		
B3LYP						
ZnO $^1\Sigma^+$	1.713	741		1.21		2.29(2.14)
ZnO $^3\Pi$	1.890	509		1.31	−0.08	
ZnO$^-$ $^2\Sigma^+$	1.780	592		1.95		
CPF[5]						
ZnO $^1\Sigma^+$	1.771	646		1.16		
ZnO $^3\Pi$	1.866	587			0.03	

[a] For ^{64}Zn and ^{16}O.

[b] The value in parentheses is corrected for the error in the O EA.

TABLE II. Summary of MCPF populations.

State	9σ		10σ		4π		net	
	Zn	O	Zn	O	Zn	O	Zn	O
ZnO $^1\Sigma^{+a}$	0.93	1.06			0.44	3.42	+0.48	−0.48
ZnO $^3\Pi$	0.55	1.40	0.84	0.15	0.10	2.85	+0.46	−0.46
ZnO^- $^2\Sigma^+$	1.28	0.63	0.63	0.37	0.34	3.54	−0.27	−0.73

[a] The $^1\Sigma^+$ state has two important configurations and the populations from the 9σ and its correlating orbital are summed.

FIGURES

FIG. 1. The MCPF 9σ natural orbital for the $^3\Pi$ state of ZnO.

FIG. 2. The MCPF 10σ natural orbital for the $^3\Pi$ state of ZnO.

FIG. 3. The MCPF 4π natural orbital for the $^3\Pi$ state of ZnO.

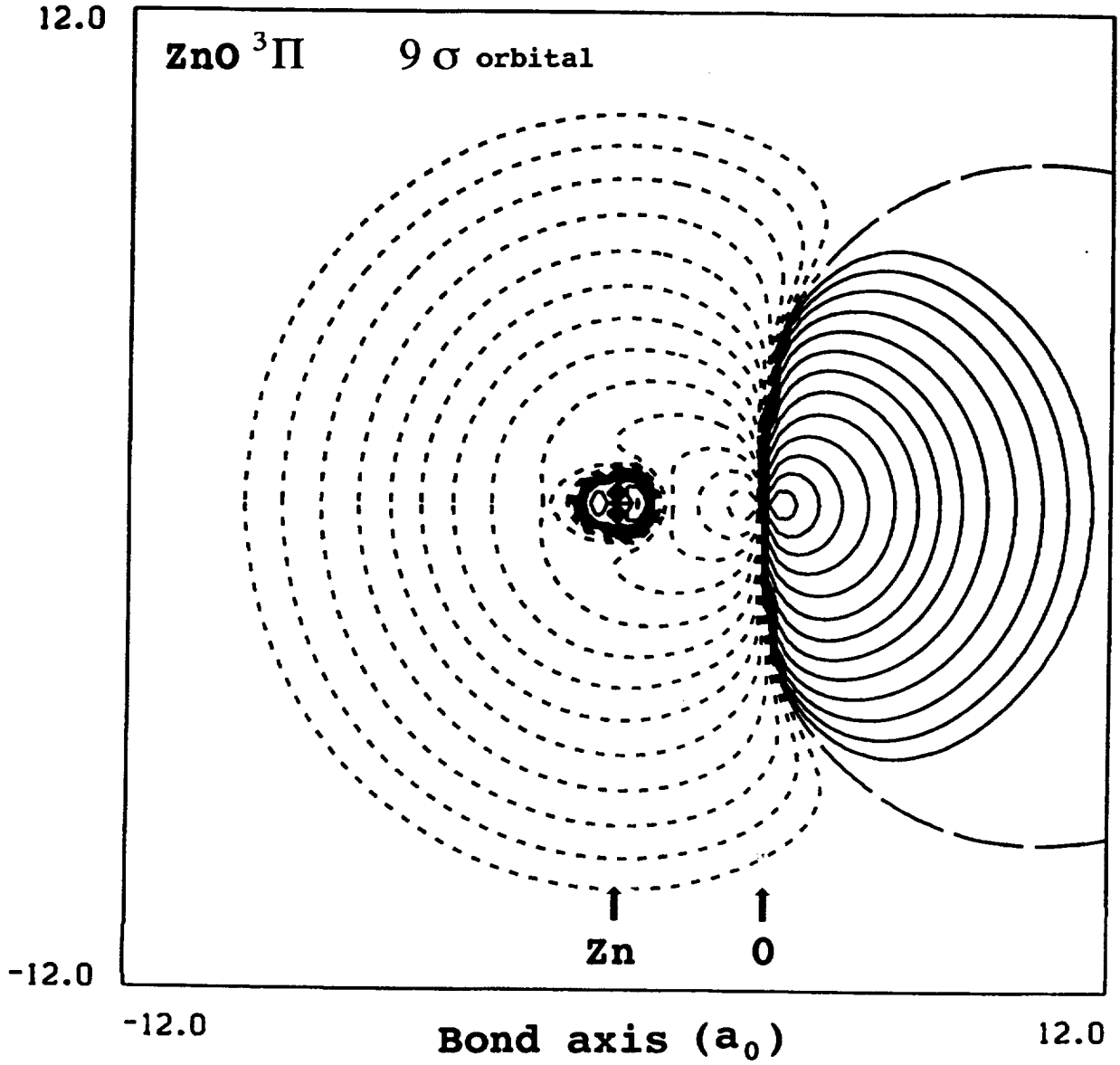
FIG. 4. The MCPF 9σ natural orbital for the $X^1\Sigma^+$ state of ZnO.

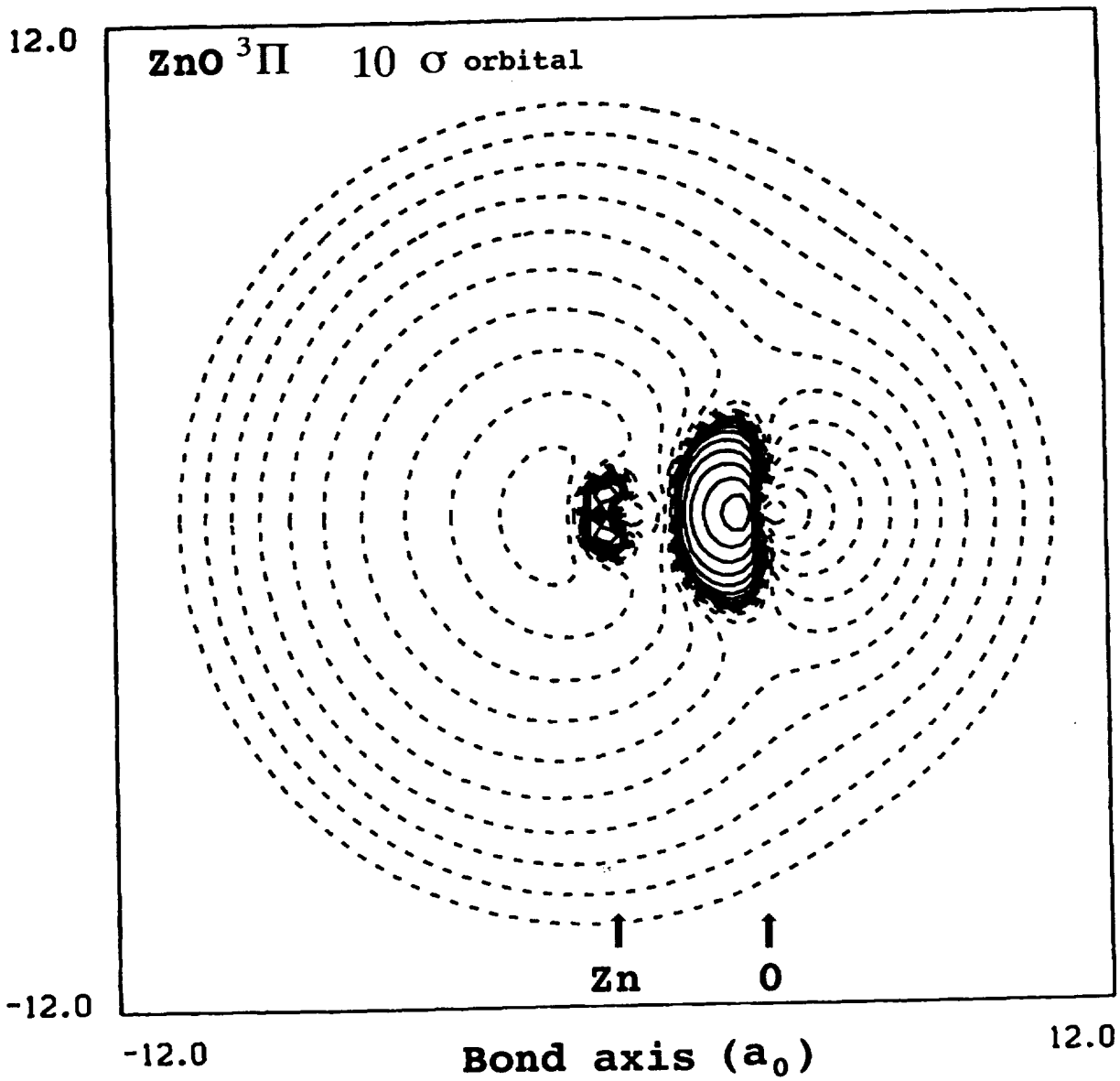
FIG. 5. The MCPF 4π natural orbital for the $X^1\Sigma^+$ state of ZnO.

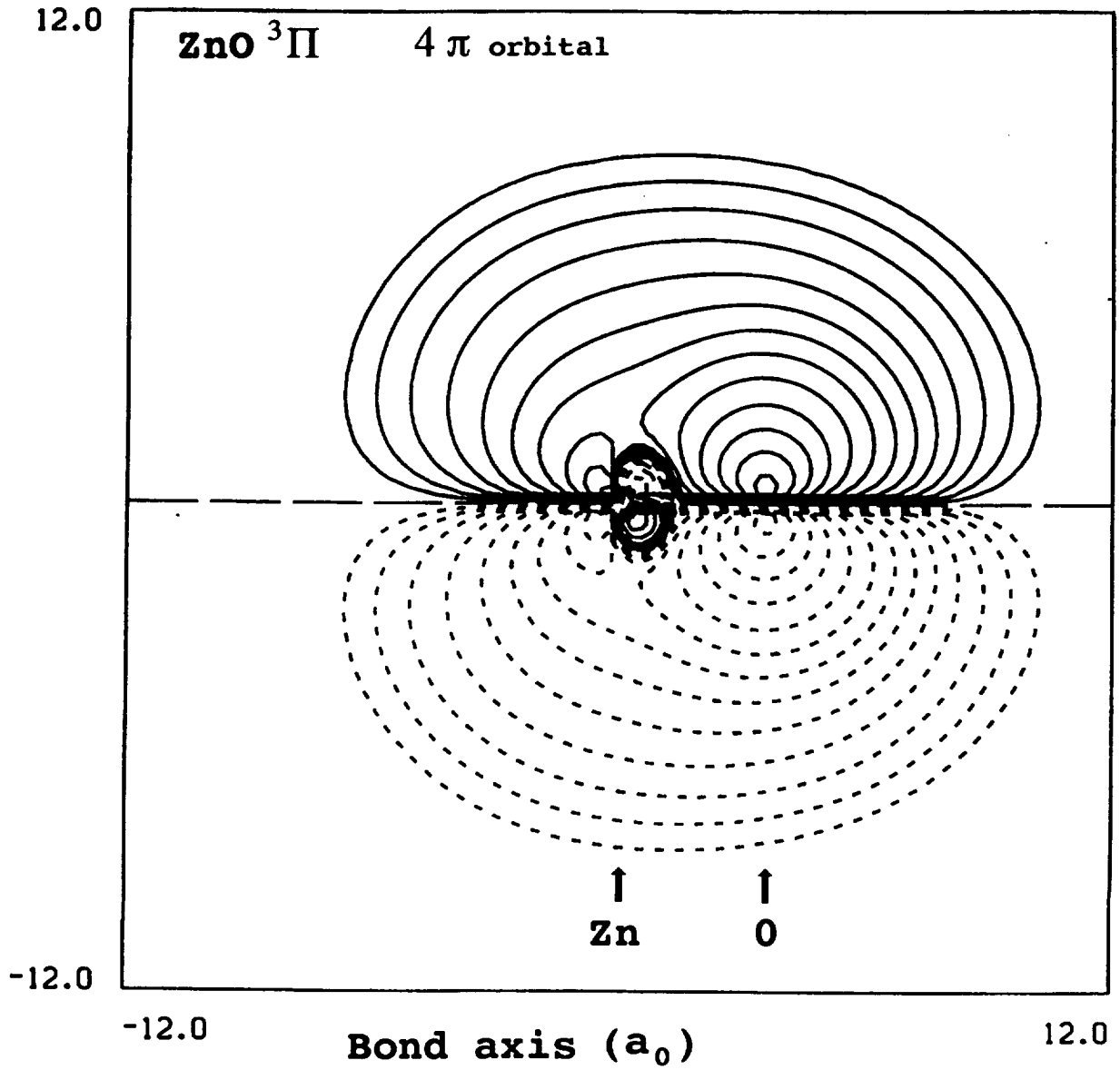
FIG. 6. The MCPF 9σ natural orbital for the $X^2\Sigma^+$ state of ZnO^-.

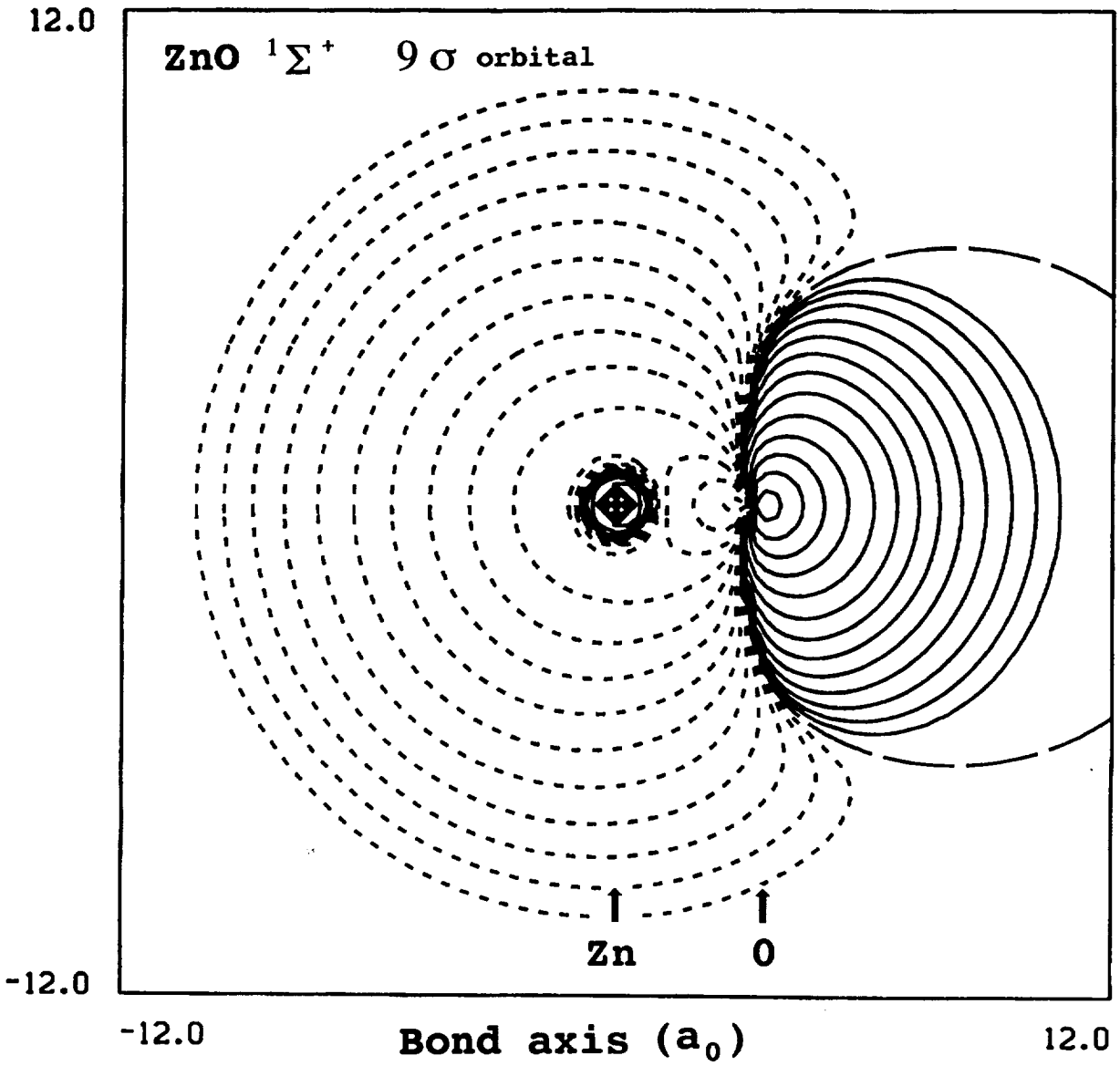
FIG. 7. The MCPF 10σ natural orbital for the $X^2\Sigma^+$ state of ZnO^-.

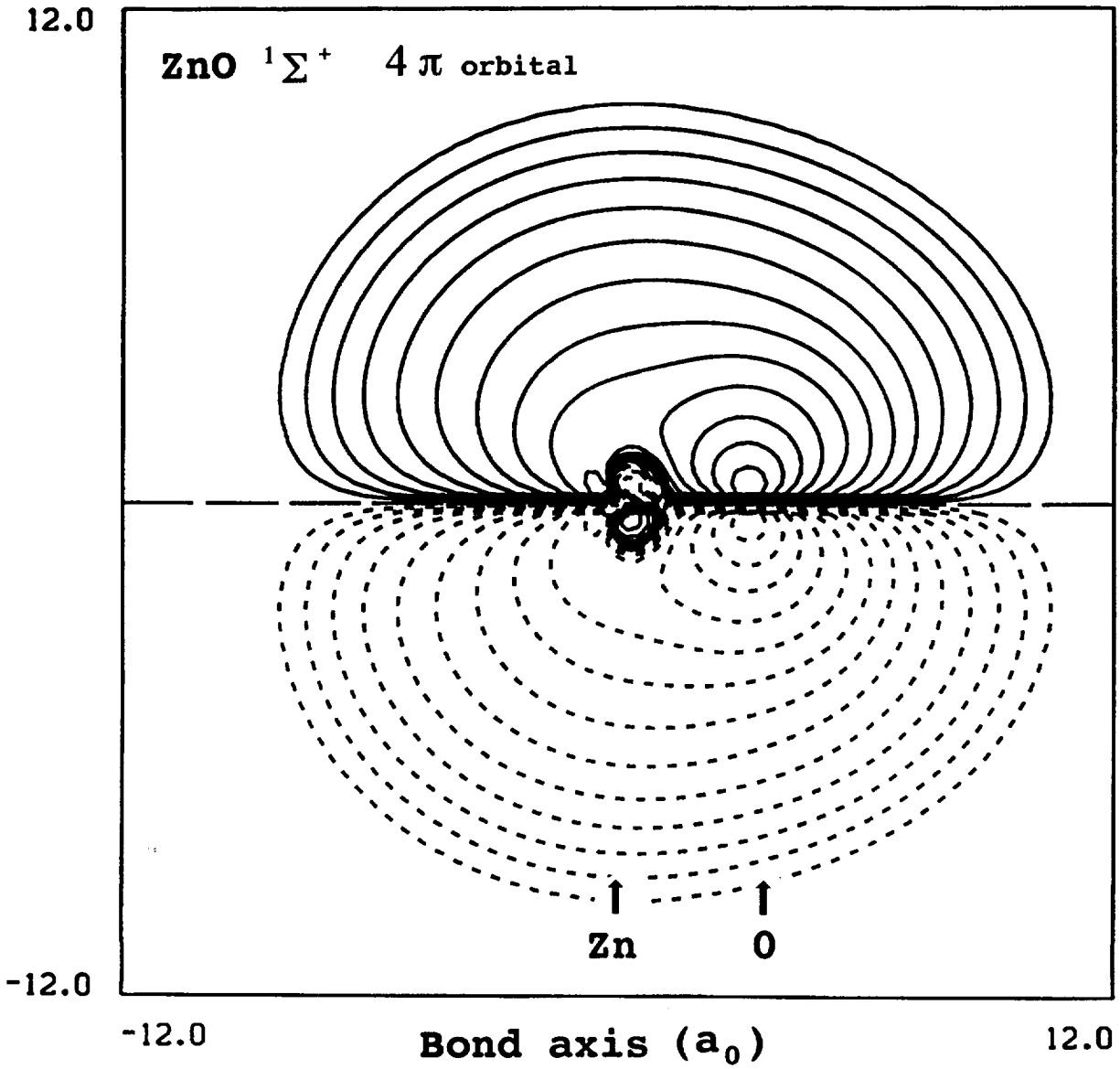
FIG. 8. The MCPF 4π natural orbital for the $X^2\Sigma^+$ state of ZnO^-.

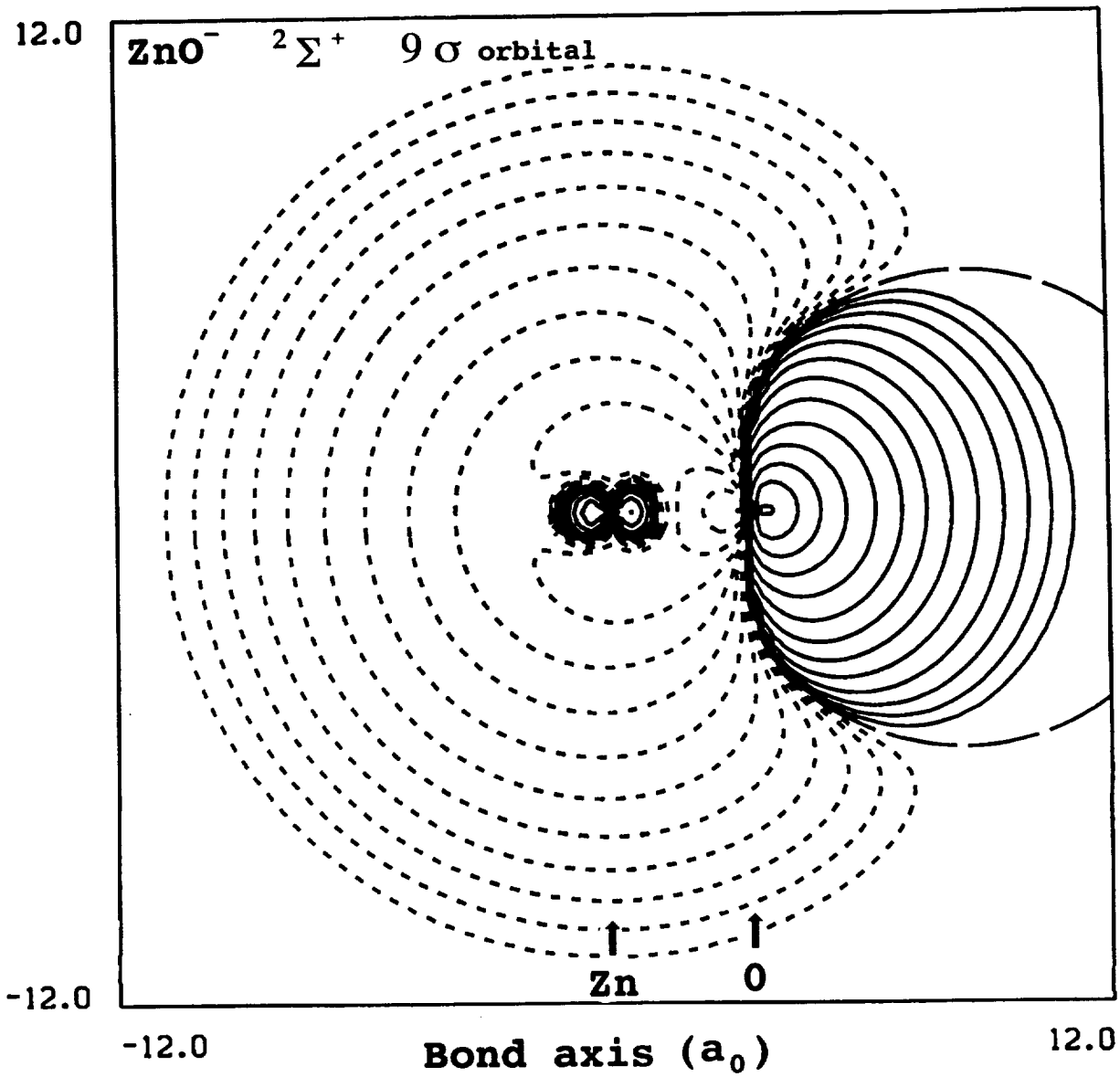

12.0
ZnO $^3\Pi$
9 σ orbital
Zn
O
-12.0
-12.0
Bond axis (a_0)
12.0

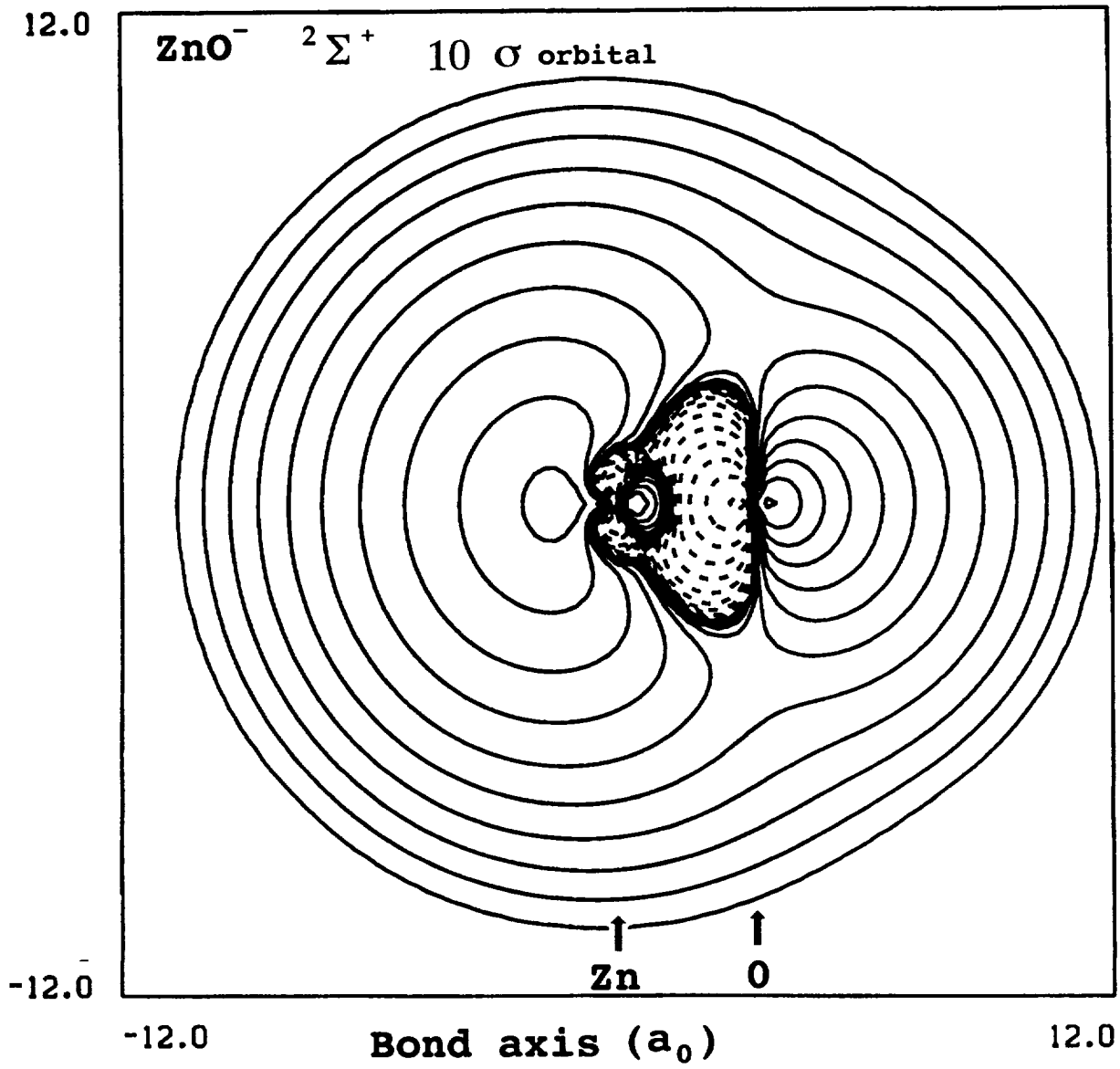

ZnO $^3\Pi$ 10 σ orbital
12.0
-12.0
-12.0
12.0
Zn
O
Bond axis (a_0)

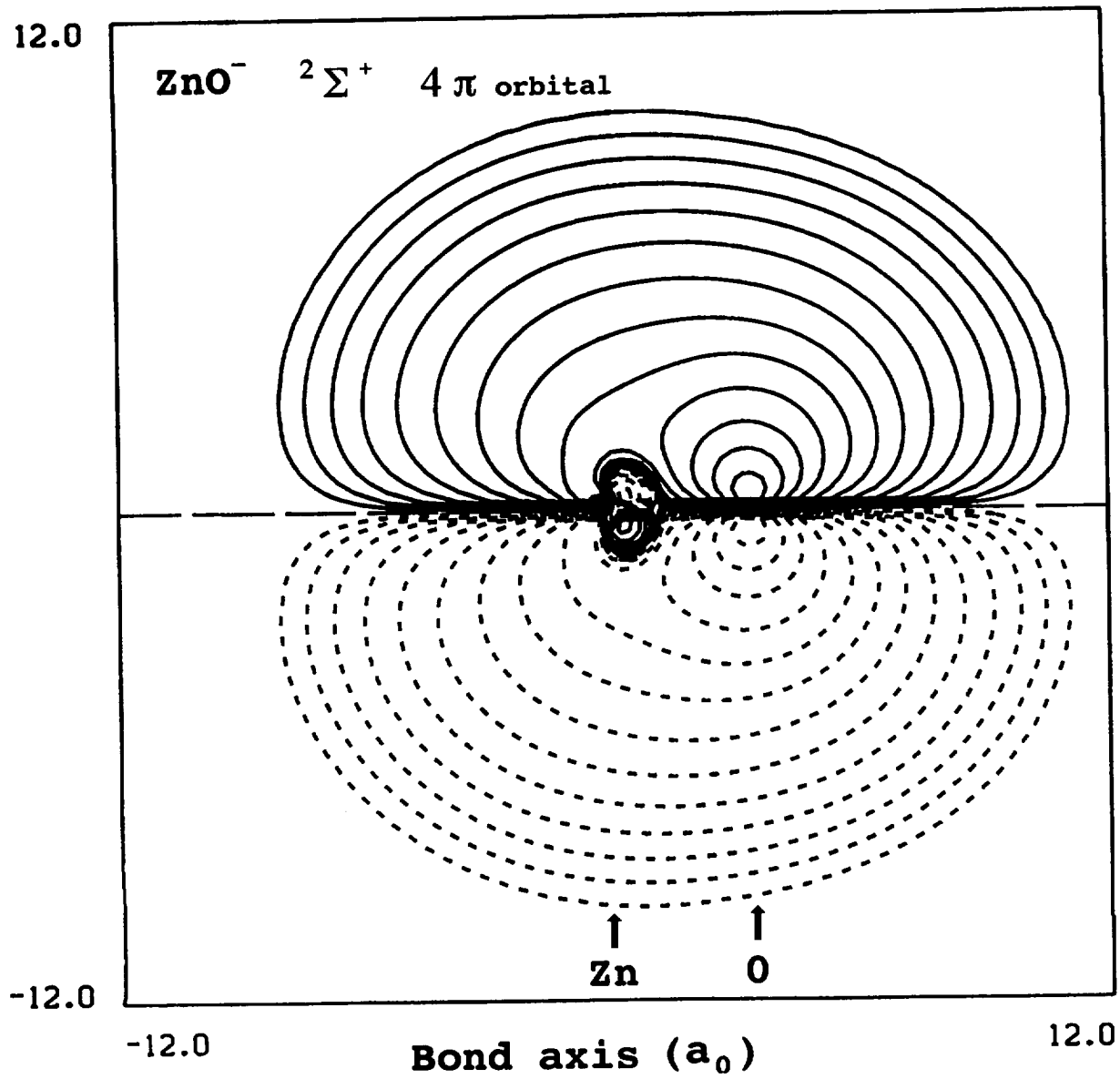

12.0
ZnO $^3\Pi$
4 π orbital
Zn
O
-12.0
-12.0
Bond axis (a_0)
12.0


12.0
ZnO $^1\Sigma^+$ 9σ orbital
Zn
O
-12.0
-12.0
Bond axis (a_0)
12.0


12.0
ZnO $^1\Sigma^+$ 4 π orbital
Zn
O
-12.0
-12.0
Bond axis (a_0)
12.0


12.0
ZnO⁻ ²Σ⁺ 9σ orbital
-12.0
Zn
O
-12.0
Bond axis (a₀)
12.0


12.0
ZnO⁻ ²Σ⁺ 10 σ orbital
-12.0
Zn
O
-12.0
Bond axis (a₀)
12.0


12.0
ZnO⁻ ²Σ⁺ 4π orbital
Zn
O
-12.0
-12.0
Bond axis (a₀)
12.0