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THE EFFECT OF ATOMIC AND EXTRA-ATOMIC RELAXATION
ON ATOMIC BINDING ENERGIES*

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Abstract:

An equivalent-cores-relaxation model is given for calculating atomic binding energies from orbital energies using only ground-state atomic properties. The agreement with experiment is excellent for the noble gases. On the basis of present knowledge of atomic relaxation, the phenomenon of "extra-atomic relaxation", in which electronic charge is attracted toward a hole-state atom, is shown to have an important effect in lowering atomic core-level binding energies in condensed phases. This will affect the interpretation of most core-level binding energies measured to date.

Siegbahn, et al.^{1,2} have given a rather complete set of experimental electron binding energies for the chemical elements, to a precision of 1 eV or better. There exist as yet relatively few theoretical values with which these

results may be compared. This Letter describes a method for estimating atomic core-electron binding energies from Hartree-Fock orbital energies plus a relaxation-energy correction that employs integrals calculated from atomic ground-state properties. The results appear to be as accurate as those obtained from hole-state calculations, especially for heavy atoms. Comparison of experimental core-level binding energies of elements with various theoretical estimates leads to the conclusion that extra-atomic relaxation amounts to several electron volts when measurements are made on molecules or condensed phases. Thus, except for the noble gases, any comparisons of available experimental binding energies of core electrons with atomic calculations should include corrections for extra-atomic relaxation.

In seeking theoretical estimates of atomic core-level binding energies, a good first approximation may be obtained by using the "orbital energies" from self-consistent field (SCF) calculations. According to Koopman's Theorem,³ the binding energy E_B of the i^{th} orbital is related to its orbital energy ϵ by

$$E_B(i) \cong \epsilon(i) \quad . \quad (1)$$

This relation is not exact because no allowance is made for relaxation of the passive orbitals toward the positive hole in the final state. As a result, the measured binding energies of atomic core levels are smaller than (minus) the corresponding orbital energies.

Bagus⁴ showed that SCF calculations could be carried out directly on the final "hole" states, yielding the total energies of these states. Binding energies could then be obtained by subtraction. Thus for the ejection of an electron from the i^{th} orbital of an atom of atomic number Z ,



the binding energy is given by

$$E_B(Z,i) = E(Z^+, \bar{i}) - E(Z) \quad . \quad (3)$$

Some difficulty might be expected in calculating the hole states, because they do not rigorously satisfy the conditions required for the Variation Principle to hold. In fact, however, Bagus found satisfactory SCF solutions for the hole states, as have subsequent workers. A major drawback of this approach is that it requires a separate SCF calculation for each hole state of each element. There is not yet available even a complete set of Dirac-Fock calculations⁵ for the elements in their ground states, so a complete set of hole-state calculations (which would require over an order of magnitude more work) seems rather distant. It would be valuable to be able to estimate core-level binding energies without hole-state calculations.

Hedin and Johansson showed⁶ that the relaxation energy,

$$E_R(i) = -\epsilon(i) - E_B(i) \quad , \quad (4)$$

can be obtained by evaluating the expectation value of a "relaxation potential",

$$V_R = \sum_{j \neq i} (V_j^* - V_j) \quad ,$$

in the i^{th} state. Here V_j represents the Coulomb plus exchange potential due to the j^{th} occupied orbital and the asterisk denotes the atomic state with a hole in the i^{th} orbital. These workers showed, specifically, that to good accuracy

$$E_R(i) = \frac{1}{2} \langle i | V_R | i \rangle \quad , \quad (5)$$

where $\langle i | V_R | i \rangle$ is given by a linear combination of Coulomb and exchange integrals. Thus

$$E_B = -\epsilon(i) - \frac{1}{2} \langle i | V_R | i \rangle \quad (6)$$

Now this result still requires knowledge of V_j^* , the potential due to the relaxed j^{th} passive orbital, for each value of j . Exact evaluation of V_j^* would necessitate hole-state calculations, but a good approximation can be obtained by using the concept of "equivalent cores". Jolly and co-workers have used this concept to estimate binding energy shifts from ground-state thermochemical data,⁷ and recently Davis and Shirley have used it to estimate relaxation energies in molecules.⁸ The essence of this approximation is that an electron in an inner orbital will almost completely shield an outer electron from one unit of nuclear charge. An outer orbital in an atom of nuclear charge Ze with a hole in an inner shell is therefore very closely approximated by the corresponding outer orbital in the ground state of the next element, of atomic number $Z + 1$. The inner orbital is contracted in element $Z + 1$, of course, but this has little effect on the inner electron-outer electron Coulomb and exchange integrals that are needed in Eq. (6).⁹ Thus it is a very good approximation to replace these hole-state integrals in element Z by the corresponding ground-state integrals in element $Z + 1$. In the notation of Slater integrals this approximation can be written as

$$F_k(n\ell, n'\ell'; Z(\overline{n\ell})^*) \cong F_k(n\ell, n'\ell'; Z + 1)$$

$$G_k(n\ell, n'\ell'; Z(\overline{n\ell})^*) \cong G_k(n\ell, n'\ell'; Z + 1) \quad (7)$$

with $n' > n$. Inner-shell relaxation ($n' < n$) and intrashell relaxation ($n' = n$), which are relatively small,⁶ are neglected in this approach. Slater¹⁰ has given expressions for the energy of interaction between electrons of angular momenta l and l' . On summing over outer shells these expressions give

$$\begin{aligned} \langle n l | V_R | n l \rangle = & \sum_{\substack{l' \\ n' > n}} \frac{N(n'l')}{(4l' + 2)} \left\{ f(l l') \Delta \left[F_0(n l, n'l') \right] \right. \\ & \left. - \Delta \sum_k \left[g_k(l l') G_k(n l, n'l') \right] \right\}, \end{aligned} \quad (8)$$

where

$$\Delta F_0(n l, n'l') \equiv F_0(n l, n'l'; Z + 1) - F_0(n l, n'l'; Z)$$

and

$$\Delta G_k(n l, n'l') \equiv G_k(n l, n'l'; Z + 1) - G_k(n l, n'l', Z) \quad . \quad (9)$$

Here $N(n'l')$ is the occupation number of the $n'l'$ subshell in the parent atom. Thus the ratio $N(n'l')/(2l' + 2)$ is the fractional occupation of this subshell; for a filled shell its value is unity. The factors $f(l l')$ and $g_k(l l')$ were obtained in an obvious way from Slater's results¹⁰: they are listed in Table 1.

The above approach was used to estimate relaxation energies for the noble gases Ne, Ar, Kr, and Xe, for which both usable orbital energies and experimental binding energies are available. Slater integrals were taken from the tables given by Mann.¹¹ To be usable for this purpose, the orbital energies

should be obtained from SCF calculations of Hartree-Fock quality,¹² and relativity should be accounted for. Rosen and Lindgren¹³ have described an optimized relativistic Hartree-Fock-Slater (HFS) method that yields orbital energies that are essentially identical to those obtained from relativistic Hartree-Fock calculations. They also used this optimized HFS method to obtain binding energies from hole-state calculations. The orbital energies and hole-state energies used below are their published values obtained by this optimized HFS method.^{1,13}

Table 2 gives the relaxation energies (E_R), the binding energies estimated on the theory given above (E_B^R), the experimental binding energies (E_B),^{1,2} and, where available, the binding energies obtained from hole-state calculations (E_B^H). The agreement of both E_B^R and E_B^H with one another and with experiment is excellent in most cases. The agreement of E_B^R with E_B^H shows that the "equivalent-core" potential model given here yields a very good estimate of the relaxation energy. A detailed analysis of the values of E_R predicted on this model is beyond the scope of this Letter, but two observations are in order. First, the model applies only to core levels; that is, to all shells inside the outermost. Second, since no account has been taken of intrashell relaxation (which Hedin and Johansson found to be relatively small), this model is expected to, and apparently does, work best for core levels of heavy atoms.

The agreement of the E_B^V values in Table 2 with experiment is actually slightly better than that of the E_B^H values. This probably arises from cancellation of errors, and it may be fortuitous. Of course no final statement can be made about atomic binding energies until the effects of electron correlation have been taken into account. We note that the large discrepancies between theory and experiment for the $1s$ orbitals in heavy atoms arises from overlarge

values of $\epsilon(1s)$, which Rosen and Lindgren attributed to quantum electrodynamic effects.

In summary, the equivalent-core potential model yields atomic binding-energy predictions in excellent agreement with experiment, especially for heavy atoms. Of the twenty-seven measured binding energies in Table 2, 16 are within 2 eV of the E_B^R predictions, and 21 are within 4 eV. In Fig. 1 the deviations of $-\epsilon$, E_B^H , and E_B^R from the experimental values are plotted against the average radius of each orbital.

Let us now use our knowledge of atomic relaxation to address the question of possible extra-atomic relaxation effects on core-level binding energies measured in condensed phases. There exists a systematic discrepancy of nearly 10 eV between the measured 1s binding energies of the second-row elements C, N, O, and F (corrected for work function) and the atomic binding energies calculated from hole-state theory. This discrepancy is illustrated in Fig. 2, in which the difference between E_B^H values from Ref. 1 and E_B are plotted. Neon, for which a gas-phase binding energy is available,² shows no such discrepancy. Before interpreting these results, let us review the reliability of atomic binding-energy estimates for these elements.

For free molecules containing the hydrides of C, N, or O, Schwartz¹⁴ gave hole-state binding energies that are within 1 eV of the experimental values. Other workers have achieved similar results in hole-state calculations of E_B work for these elements in free molecules.

Let us now consider carbon specifically. The 1s binding energy in atomic carbon can be estimated in three ways. First, hole-state estimates give $E_B^H = 297 \text{ eV}^1$. Second, the theory described above can be used to estimate

$E_R = 8.6$ eV, which can then be combined with Mann's $-\epsilon(\text{Cls}) = 308.5$ eV¹¹ to yield $E_B^V = 300$ eV. Finally, Siegbahn et al.² fitted the C(1s) binding energies of carbon in several small molecules to the equation $E_B = kq + V + \lambda$. Setting q and V equal to zero, their equation would give $E_B = 291.4$ eV for the binding energy of a neutral carbon atom in a small molecule. Davis and Shirley⁸ have found that the core-hole charge of +1 in such a molecule is essentially completely shielded by transfer of electronic charge, through relaxation, from the ligand atoms. Assuming that the electronic charge is transferred into the C(2p) shell, the extra-atomic relaxation energy can be estimated as

$$\Delta V \cong F_0(1s,2p) - \frac{1}{6} G_1(1s,2p) - e^2/R \cong 7.5 \text{ eV} ,$$

if the internuclear distance $R = 1.1$ Å of methane is used. Thus the C(1s) free-atom binding energy would be about $291.4 + 7.5 = 299$ eV. This estimate, while crude, is physically sound, and it agrees well with the above two values of $E_B(\text{Cls, free atom})$. We are therefore led to the conclusion that the free-atom C(1s) binding energy is in the range 297 - 300 eV, or very close to this range. The measured binding C(1s) energy in graphite is 284 eV. After correction for the work function, this becomes $E_B(\text{Cls, graphite}) = 288$ eV relative to the vacuum level. A discrepancy of about 10 eV thus clearly exists for carbon. Similar considerations lead to discrepancies of about this size for the other second-row elements, as Fig. 2 indicates. We attribute this discrepancy to extra-atomic relaxation accompanying photoemission in the solid state.

Relaxation during photoemission may be understood as the natural consequence of minimizing the emitting system's Coulombic energy. In a free atom, the passive orbitals relax adiabatically, and the relaxation energy can

be estimated as discussed above. If the atom were a classical system, and charge were continuous, it would be natural to describe this relaxation in terms of the outward diffusion of a quantity of charge of value $+e$, suddenly introduced near center of the atom, in order to reduce the Coulombic repulsion energy. This picture facilitates an understanding of extranuclear relaxation molecules and solids. Thus Davis and Shirley found that the charge distribution in CH_4^+ immediately following emission of a $\text{C}(1s)$ electron is approximately given by a neutral carbon atom and charges of $+e/4$ in each hydrogen, while in diatomic molecule ions such as CO^+ each atom has a charge of about $+e/2$ following ejection of a $\text{C}1s$ electron.⁸ In fact, the $1s$ -electron binding energies of diatomic molecules and hydrides lie between the theoretical free-atom values and the measured solid-phase values (Fig. 2), and in the order expected on the basis of extra-atomic relaxation: $E_B(\text{free atom}) > E_B(\text{diatomic}) > E_B(\text{hydride}) > E_B(\text{solid})$. This order follows because a charge of about $+e/2$ is left on the host atom in a diatomic molecule, while in a hydride the positive charge can migrate to the hydrogen ligands (these two types of molecules are the simplest to consider here because in them the host atoms are nearly neutral in the initial states). In a solid sample the positive charge can migrate farther than the nearest ligand during photoemission, thereby further reducing the core-electron binding energy. This effect accounts for the reduction of $E_B(\text{C}1s, \text{graphite})$ below $E_B(\text{C}1s, \text{CH}_4)$, for example. Similar results should obtain for other solids.

Having once established the importance of extra-atomic relaxation in relation to core-level binding energy measurements on condensed phases, we note that this phenomenon may be the key factor in understanding several previously unexplained observations. For example, core electron binding energies of

noble gases embedded in metallic foils¹ were in most cases 2-5 eV higher than those of the same orbitals studied with gas-phase samples.² Shifts of about 3 eV have also been observed in molecules between the gas and solid phase. Thus Siegbahn et al.² found that the N1s binding energies of aminobenzene and nitrobenzene are, respectively, 3.1 eV and 2.4 eV higher in the solid phase. This shift can be tentatively attributed to "extramolecular relaxation" due to polarization of neighboring molecules in the solid.

Extra-atomic relaxation has broad implications for all atomic binding energies obtained from data taken on solids. Because the relaxation is a property of the hole state rather than of the photoelectric process per se, it affects binding energies obtained from x-ray data, such as those tabulated by Bearden and Burr.¹⁵ It will be of interest both to estimate the corrections that must be applied to calculated free-atom binding energies before they can be compared to experiment and to measure binding energies in free atoms of more elements. As for further applications of extra-atomic relaxation, it seems probable that the relaxation energy accompanying photoemission of a core electron from an absorbed atom or molecule will depend on the nature of the substrate as well as on the nature of the binding between adsorbate and substrate. Thus extra-atomic relaxation may play a role in elucidating the adsorption process.

FOOTNOTES AND REFERENCES

* Work performed under the auspices of the U. S. Atomic Energy Commission.

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Table 1. The f and g Coefficients in Eq. (9)

l	l'	$f(ll')$	$g_0(ll')$	$g_1(ll')$	$g_2(ll')$	$g_3(ll')$	$g_4(ll')$	$g_5(ll')$	$g_6(ll')$
0	0	2	1						
0	1	6		1					
0	2	10			1				
0	3	14				1			
1	0	2		1/3					
1	1	6	1		2/5				
1	2	10		2/3		3/7			
1	3	14			3/5		4/9		
2	0	2			1/5				
2	1	6		2/5		9/35			
2	2	10	1		2/7		2/7		
2	3	14		3/5		4/15		10/33	
3	0	2				1/7			
3	1	6			9/35		4/21		
3	2	10		3/7		4/21		25/77	
3	3	14	1		4/15		2/11		100/429

Table 2. Noble Gas Core-Electron Binding Energies (eV)

Orbital	$E_R^{(a)}$	$E_B^{H(b)}$	$E_B^{R(c)}$	$E_B^{(d)}$
Ne 1s	25.6	870	868.4	870.2
Ar 1s	37	3209	3203	3205.9
Ar 2s	10.5	327	325.5	326.3
Ar 2p _{1/2}	11	250	251	250.6
Ar 2p _{3/2}	11	248	248	248.5
Kr 1s	59	14358	14351	14326
Kr 2s	32	1933	1926	1924.6
Kr 2p _{1/2}	32	1735	1730	1730.9
Kr 2p _{3/2}	32	1681	1676	1678.4
Kr 3s	7	296	297	292.8
Kr 3p _{1/2}	7	225	226	222.2
Kr 3p _{3/2}	7	217	218	214.4
Kr 3d _{3/2}	7	93	94	94.9
Kr 3d _{5/2}	7	92	93	93.7
Xe 1s	72	34689	34684	34561
Xe 2s	44	5472	5462	5453.2
Xe 2p _{1/2}	44		5115	5107.2
Xe 2p _{3/2}	44		4789	4787.4
Xe 3s	18		1150	1148.7
Xe 3p _{1/2}	18		1005	1002.1
Xe 3p _{3/2}	18		941	940.6
Xe 3d _{3/2}	19		687	689.0
Xe 3d _{5/2}	19		674	676.4
Xe 4s	4.8		224	213.2
Xe 4p _{1/2}	4.8		170	--
Xe 4p _{3/2}	4.8		157	145.5
Xe 4d _{3/2}	4.8		68.3	69.5
Xe 4d _{5/2}	4.8		66.2	67.5

(continued)

Table 2. (continued)

^aEstimated using Eqs. (5) - (9), and integrals from Ref. 11.

^bFrom Refs. 1 and 13.

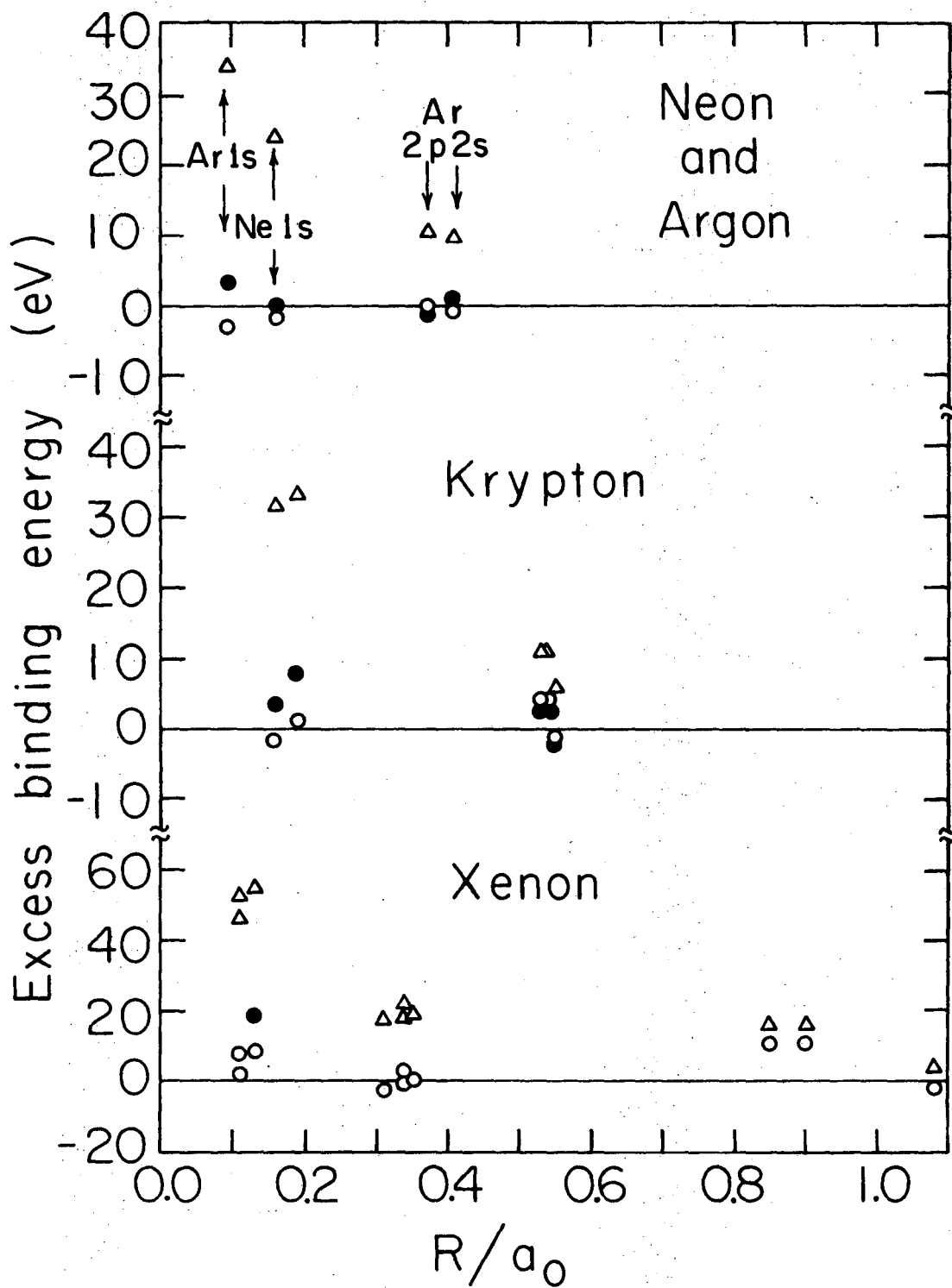
^cThe orbital energies for these estimates were taken from Refs. 1 and 13.

^dFrom Refs. 1 and 2.

FIGURE CAPTIONS

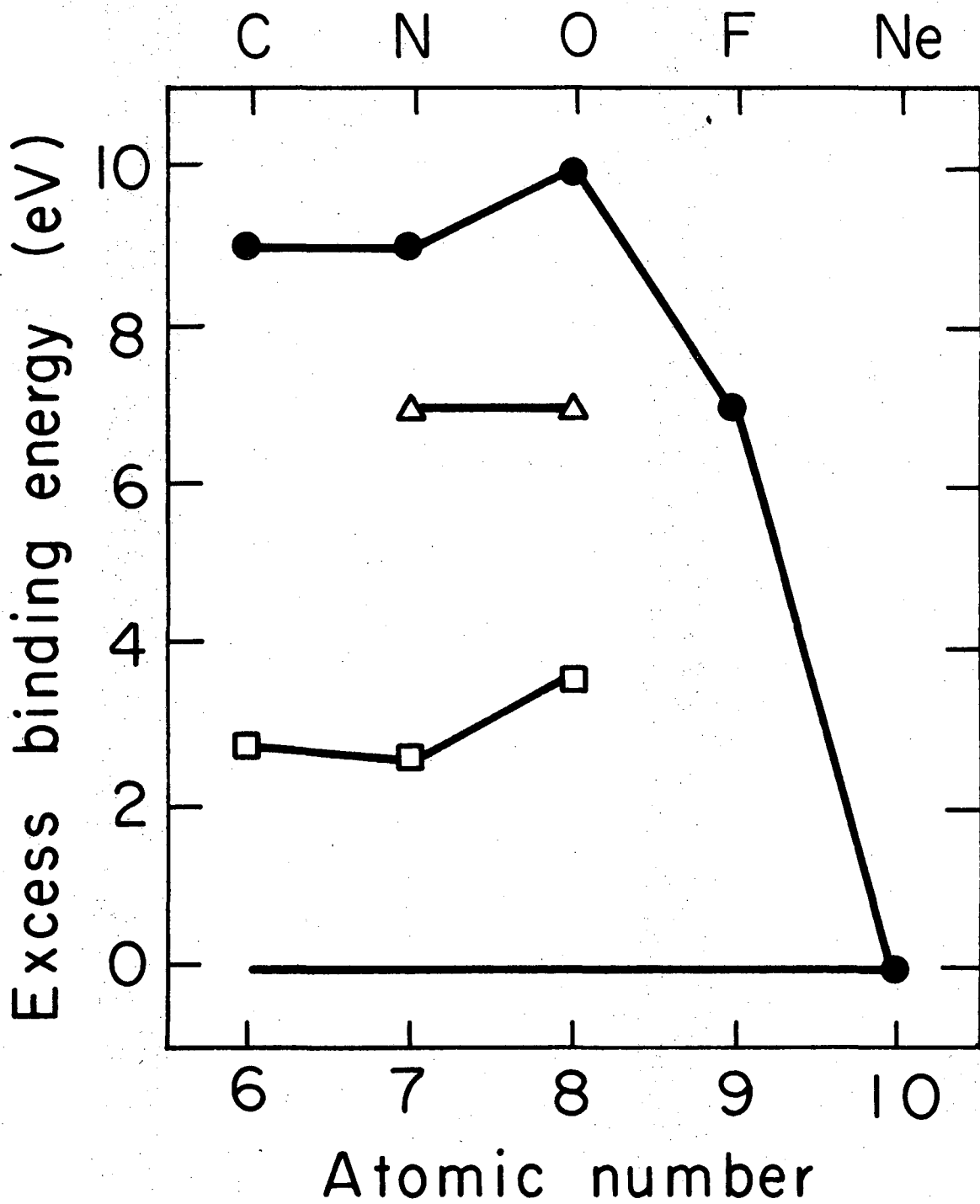
Fig. 1. Plots of the deviations of theoretical binding energies from experiment for four rare gases, using orbital energies (Δ), hole-state energies (\square), and the method described herein (\circ). The abscissa is the orbital radius in atomic units. The Xe 1s values are not shown.

Fig. 2. The binding-energy discrepancy for 1s orbitals of second-row elements in solids. Filled circles represent $E_B^H(\text{atomic}) - E_B(\text{expt.})$. Only the neon point is a gas-phase result. Triangles and squares show excess binding energies (over the experimental values in solids) for gaseous diatomics and hydrides, respectively.



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Fig. 1



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Fig. 2

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