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Atomic and molecular 2*p* binding energies of P, As, and Se from many-body calculations and x-ray photoelectron spectroscopy

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The $2p_{1/2,3/2}$ levels in As_4 and the $2p_{3/2}$ level in $Se_{5,6}$ have been measured by x-ray photoelectron spectroscopy with the use of 1486.6-eV (Al$K\alpha$) radiation. The $2p_{1/2}$ binding energies have been calculated for the atomic species, as well as for atomic phosphorus, as the difference between the total energies of the $2p_{1/2}$ hole state and the ground (neutral) state ΔSCF (Δ self-consistent field method), using the Dirac-Fock program of Desclaux, to which is added the respective correlation-energy difference between the two states. The calculated values of 140.70 eV for P $2p_{1/2}$, 1368.89 eV for As $2p_{1/2}$, and 1484.88 eV for Se $2p_{1/2}$ include a 0.7–1.0-eV increase due to the effects of correlation, consistent with earlier work done on the K and Zn atoms. The $2p_{3/2}$ atomic binding energies were calculated similarly with the use of available Dirac-Slater ΔSCF values. When we combine these with the measured molecular binding energy of P_4, As_4, and $Se_{5,6}$ we obtain corresponding 2*p* chemical shifts (atom-molecule) of 3.5, 3.0, and 2.4 eV, respectively. Comparison is also made between the atomic, molecular, and solid-state binding energies of As and Se, and it is found that the solid-state binding energy is the lowest of the three in both cases, as expected from consideration of extra-atomic relaxation.

I. INTRODUCTION

One of the important goals of x-ray photoelectron spectroscopy (XPS) should be the determination of binding-energy shifts with increase in cluster size. The shift between the species at the extremes of the progression, the atom, and the (infinite) solid, has received considerable attention. The recent availability of atomic binding energies from XPS as well as other techniques has aided significantly in the study of phase transition shifts. On the other hand, solid-state XPS data are available for a large number of solids and the experimental situation is generally quite satisfactory.

In contrast, the experimental study of homonuclear dimers, trimers, etc., by XPS remains elusive, partly due to the difficulty of producing sufficient number densities of these species for study by gas-phase XPS. Progress in this area will depend on the combination of the latest instrumental developments for improving both the resolution and the intensity with the techniques of high-temperature supersonic beams. Synchrotron radiation may be used in the future for such studies.

This work represents an effort in the direction of studying the evolution of core binding energies with size. We determine the binding energies in the atoms and in one of the homonuclear species. The choice of the latter is dictated by the molecular form of the elemental vapor in each case. Under the conditions of gas-phase XPS, the elements usually vaporize predominantly in atomic form or as one of the homonuclear species. For example, we have previously studied Te_2 and Sb_4 and the study of the systems discussed here is also part of our continuing efforts in high-temperature gas-phase XPS. To obtain the atomic values we performed state-of-the-art binding-energy calculations, including the effects of correlation. Thus our results should give reliable absolute binding energies rather than merely binding-energy shifts such as those calculated using semiempirical methods [complete neglect of differential overlap (CNDO), etc.].

In Sec. II, we describe the method used to calculate the atomic binding energies, which includes to a satisfactory approximation, the effects of both correlation and relativity. For the former, we introduce in this work a new method, called BCB (Bartlett-Condon-Beck), of constructing *LS* eigenstates which is highly suitable for treating the large number (~ 1000) of Slater determinants which arise in our method[1,2] when *p* binding energies are calculated to high accuracy (~ 0.1 eV) or whenever *d* or *f* electrons are removed and the residual core possesses an open-shell structure.

Contrary to other cases we have investigated lately[3,4] for the 2*p* binding energies (BE), *initial*-state correlation effects dominate and are of modest size (~ 1 eV), as had been anticipated in our earlier survey.[5] We present direct evidence that when SEOS-like (symmetric exchange of symmetry)[3] correlation effects involve off-shell substitutions, as for the replacement $3d^2 \rightarrow 2p\epsilon f$, their magnitude drastically decreases. Since the hole state is embedded in the continuum corresponding to the above process, we treat it using the method of configuration interaction in the continuum[6] (CIC) which is based on the work of Fano[7] and Altick.[8]

Experimental details and the measured molecular binding energies are given in Sec. III. Our atomic and molecular results are compared to each other and to the binding energies in the solid in Sec. IV.

II. THEORETICAL METHOD AND RESULTS

Assuming that the experiment is done at a high enough energy so that postcollisional events are minimized (for a recent discussion of when they are important see Ref. 9), atomic binding energies may be defined in terms of differences (Δ) of total energies of stationary or nonstationary atomic states. State-of-the-art results suggest that BE can be broken up into several contributions as follows:

$$E_B = \Delta E_{\rm DF} + \Delta E_{\rm NR\text{-}cor} + \Delta E_{\rm rel\text{-}cor} + \Delta E_{\rm rad} \ , \tag{1}$$

where $\Delta E_{\rm DF}$ is the Dirac-Fock contribution obtained by subtracting the total energies and includes the average Breit interactions, as obtained with the program of Desclaux.[10] This is the main contribution to E_B. The values obtained for P $2p$, As $2p$, and Se $2p$ are shown in Table III, column 3, and will be discussed below. The version of Desclaux's program that we have cannot be used for a system with two open shells of the same symmetry. Since the atoms considered in this work have an open valence $p_{3/2}$ shell, the $2p_{3/2}$ binding energies could not be calculated. They were instead obtained from the Dirac-Slater (DS) work of Huang *et al.*[11] and are given in column 2 of Table III. It appears that the DS results are always below the Dirac-Fock (DF) values,[12] but the difference for the levels considered here is small (0.3 eV or less). Accordingly, we have corrected the $2p_{3/2}$ DS binding energies by the difference between DS and DF for the $2p_{1/2}$ levels. The results are shown in column 3 of Table III.

The sum $\Delta E_{\rm NR\text{-}cor} + \Delta E_{\rm rel\text{-}cor}$ represents the entire correlation effect, which in principle, would be obtained within the context of a comprehensive relativistic correlation theory. Since none that is capable of the sophistication required here appears to exist yet, we follow past work and assume that $\Delta E_{\rm rel\text{-}cor} = 0$, thus evaluating the correlation energy nonrelativistically. The good agreement (e.g., Refs. 3 and 4) between theory and experiment gives us some confidence that such a procedure is viable, at least for electrons having moderate binding energies.

The remaining term of Eq. (1) $\Delta E_{\rm rad}$ represents the radiative corrections to the BE, which are known to decrease as n or l increases (we are removing the nl_j electron). This is fortunate, as radiative effects for non-s electrons are currently difficult to estimate.[13] In this work, we take $\Delta E_{\rm rad} = 0$ for the np BE.

The principal theoretical work required here is then to evaluate $\Delta E_{\rm NR\text{-}cor}$. To do this, we begin with a reference function Φ, which may be single or multiconfigurational and which we obtain from the Froese Fischer program.[14] Subshells contained in Φ are designated s and those nearly degenerate with them, as $\bar{s}$. The union of these two sets is called the Fermi sea (FS), of which general examples have been given elsewhere.[2] The remaining one-electron functions needed to complete the space are called virtuals v and are orthogonal to the FS functions. The *form* of the correlation function X is then dictated by first-order perturbation theory, expressed in subshell form. We thus speak of promoting one or two subshells (s) into open subshells (s^* or v) as follows:

$$s \rightarrow s^* \ \ \text{(FS polarization)} \ , \tag{2a}$$

$$ss' \rightarrow s^* s^{*\prime} \ \ \text{(internal)} \ , \tag{2b}$$

$$s \rightarrow v \ \ \text{(virtual polarization)} \ , \tag{2c}$$

$$ss' \rightarrow s^* v \ \ \text{(hole virtual)} \ , \tag{2d}$$

$$ss' \rightarrow vv' \ \ \text{(bivirtual)} \ , \tag{2e}$$

where s^* is either an $\bar{s}$ or an open s subshell.

The above characterization is often very valuable[3-5] for analysis purposes, and can correspond to actual physical processes (e.g., Coster-Kronig events). The configurational coefficients and radial parts are then determined[1] by application of the energy variational principle.

The calculation implied by Eqs. (2), which does not include the complication of triple and quadruple excitations whose role in at least the atomic negative ions is significant,[15] is still essentially too complicated [several thousands of determinants would be involved principally arising from Eq. (2e)] to carry out at the full configuration-interaction (CI) level. Fortunately, experience has shown that the major part of the correlation energy is common to both states when neutral or positively ionized systems are involved, and that we need only compute those parts which are significant and either are unique to one of the two states or are strongly dependent on the effective charge. For the $2p$ BE considered here, the contributions which must be calculated are shown in Table I.

The BCB Method. In our approach, X is expanded in N-electron symmetry-adapted functions (SAF's) which have a unique parity L,S,M_L,M_S and associated parentage where necessary. Formerly,[1] these SAF's have been constructed by simultaneously diagonalizing the S^2 and L^2 matrices, which requires the use of an efficient large-scale multiple-root diagonalizer program. However, configura-

TABLE I. Configurations included in initial and final states used to calculate the nonrelativistic correlation contribution to the $2p$ BE.[a]

Unique to	
Initial state[b]	Final state
$2p^2 \rightarrow v_l^2 + v_{\bar{l}} v_{\bar{l}+2}$ $(l \leq 3, \bar{l} = 0,1)$	$2s \rightarrow v_d$
$ms\,2p \rightarrow v_l v_{l+1}$ $(l \leq 3,\ m \leq 4)$	$2p \rightarrow v_f$
$2p\,3p \rightarrow v_l^2 + v_l v_l' + v_s v_d$ $(l \leq 3)$	$2s\,3s \rightarrow 2pv_p$
$2p\,3d \rightarrow v_l v_{l+1}$ $(l \leq 3)$	$2s\,3p \rightarrow 2p\ (v_s + v_d)$
	$2s^2 \rightarrow 2pv_p$
Common to both states[c]	As and Se only
$ns \rightarrow v_d$	$3s \rightarrow d$
$np \rightarrow v_f$	$3d \rightarrow v_g$
$ns^2 \rightarrow npv_p$	$3p \rightarrow v_f$
$np^2 \rightarrow v_l^2 + v_{\bar{l}} v_{\bar{l}+2}$ $(l \leq 3\ \bar{l} = 0,1)$	$2s\,3d \rightarrow 2p\ (v_p + v_f)$
$nsnp \rightarrow v_l v_{l+1} (l \leq 2)$	$3d^2 \rightarrow 2p\epsilon f$[d]

[a] Expressed in terms of subshell excitations from Φ, the reference function. The subscript on v refers to the orbital angular momentum, and the primes are used to distinguish virtuals of a common section having different radial functions (virtuals belonging to different sections and/or states also generally have different radial functions).

[b] A portion of these effects are also contained in the final state. However, it is possible to extract the differential correlation contribution by solely examining the ground state (see text).

[c] These are the valence-shell correlation effects ($n = 3$ for P, and $n = 4$ for As and Se) which are significantly dependent on the effective charge, and hence must be computed separately for each state.

[d] This excitation requires special treatment (see text).

tions such as that generated from the $2p\,3d \rightarrow v_f v_g$ substitution (in As, for example) possess several hundreds (~ 600 here) of determinants, making them inaccessible to most current diagonalizer programs.

To avoid the dependence on such algorithms, we use a method to construct SAF's first introduced by Bartlett[16] which we had used earlier[17] to construct three-electron SAF's, following the work of Condon and Shortley.[18] Let us, for the sake of illustration, divide the configuration into two parts, I and II, with no subshell being found in both sections. If we construct, e.g., $S_{\mathrm{I}},L_{\mathrm{I}},M_{L_{\mathrm{I}}},M_{S_{\mathrm{I}}}$ eigenstates for part I, designated $\chi_{\mathrm{I}}(S_{\mathrm{I}},L_{\mathrm{I}},M_{L_{\mathrm{I}}},M_{S_{\mathrm{I}}})$ (in practice we do this for $M_{\mathrm{I}}=L_{\mathrm{I}}$, $M_{S_{\mathrm{I}}}=S_{\mathrm{I}}$ by the earlier method and use step-up or -down operators to generate other M_S,M_L combinations, so as to have a consistent phase convention), then the N-electron SAF desired, $\chi(S,L,M_L,M_S)$ is

$$\chi(S,L,M_L,M_S)=[(2S+1)(2L+1)]^{1/2} \times \sum_{M_{L_{\mathrm{I}}},M_{L_{\mathrm{II}}}} \sum_{M_{S_{\mathrm{I}}},M_{S_{\mathrm{II}}}} \begin{pmatrix} S_{\mathrm{I}} & S_{\mathrm{II}} & S \\ M_{S_{\mathrm{I}}} & M_{S_{\mathrm{II}}} & -M_S \end{pmatrix} \begin{pmatrix} L_{\mathrm{I}} & L_{\mathrm{II}} & L \\ M_{L_{\mathrm{I}}} & M_{L_{\mathrm{II}}} & -M_L \end{pmatrix} \chi_{\mathrm{I}}(S_{\mathrm{I}},L_{\mathrm{I}},M_{L_{\mathrm{I}}}M_{S_{\mathrm{I}}})\chi_{\mathrm{II}}(S_{\mathrm{II}},L_{\mathrm{II}},M_{L_{\mathrm{II}}},M_{S_{\mathrm{II}}}) , \tag{3}$$

where the $3j$ symbols are subjected to the usual[19] restrictions on their argument. If $\Delta_{\mathrm{I}}(n_1,l_1,m_{l_1},m_{s_1};\ldots;n_k,l_k,m_{l_k},m_{s_k})$ represents a determinant of χ_{I} and $\Delta_{\mathrm{II}}(n_{k+1},l_{k+1},m_{l_{k+1}},m_{s_{k+1}};\ldots;n_N,l_N,m_{l_N},m_{s_N})$ a determinant of χ_{II}, the N-electron determinant formed from the product of the two, is simply

$$\Delta_{\mathrm{I+II}}(n_1,l_1,m_{l_1},m_{s_1};\ldots;n_k,l_k,m_{l_k},m_{s_k};n_{k+1},l_{k+1},m_{l_{k+1}},m_{s_{k+1}};\ldots;n_N,l_N,m_{l_N},m_{s_N}) .$$

After the N-electron SAF's are created (construction times are two orders of magnitude smaller for the larger matrices than if diagonalization methods were used), a new procedure is implemented to store and compare the determinants, which if left fully unpacked could occupy 100 000 locations or so. Here, we "*bit* pack" the FS part of each determinant (two words are used, so that the FS must consist of fewer than 64 spin orbitals), turning the bit on if the FS spin orbital is occupied, and we "*byte* pack" the virtual space (into one word), with the actual virtual spin-orbital number. [Here 1 byte≡8 bits (binary digits).] Thus three words (≡12 bytes) are required to store any one determinant. Comparisons on the HF part of the determinant are done in a linear fashion, bit by bit. The virtual parts are then unpacked and compared as usual.[1,20] This speeds up construction of the "Slater-energy—matrix tables" considerably, in which each energy matrix element is expressed in terms of one- and two-electron radial integrals, and computation then proceeds normally,[20] with the results for the $2p$ binding energies of P, As, and Se shown in Table II.

TABLE II. Differential correlation-energy contributions to the $2p$ BE (eV).[a]

Type	P	As	Se
$1s\,2p$ bivirtual	0.124	0.140	0.153
$2s\,2p$ bivirtual	0.268	0.207	0.205
$2p^2$ bivirtual	1.673	1.415	1.398
$2p\,3s$ bivirtual	0.062	0.035	0.034
$2p\,3p$ bivirtual	0.090	0.203	0.203[b]
$2p\,3d$ bivirtual		0.389	0.389[b]
$2p\,4s$ bivirtual		0.004	0.001
$2p\,4p$ bivirtual		~ 0	~ 0
Unique to final state[c]	-0.990	-1.586	-1.594
Net valence shell correlation[d]	-0.241	-0.100	-0.073
Total[e]	$+0.986$	$+0.707$	$+0.716$

[a] For both the initial and final states, the *term* of lowest energy was used.

[b] Transferred from As.

[c] See footnote b of Table I.

[d] See footnote c of Table I.

[e] A sum of all numerical entries in this column.

For each configuration, the virtuals were represented with two optimized Slater-type orbitals (STO's). It appears that the various approximations may introduce total uncertainties of $\sim$0.2—0.3 eV. Combining these results with the DF values obtained separately and listed in Table III, column 3, we obtain for the atomic $2p_{1/2}$ BE 140.70, 1368.89, and 1484.88 eV, for P, As, and Se, respectively. The values for the $2p_{3/2}$ binding energies were obtained using corrected DS Δ SCF (Δ self-consistent-field) binding energies as explained above. From previous work,[12] however, the discrepancy between DF and DS appears to be larger for the $l+\frac{1}{2}$ spin-orbit component than for the $l-\frac{1}{2}$ component. If the calculated[12] Zn $2p$ binding energies are used to obtain the added $2p_{3/2}$ correction for As and Se, the $2p_{3/2}$ BE's would be increased by 0.15 eV; that is, As $2p_{3/2}$ would be 1332.98 eV and Se $2p_{3/2}$ would be 1443.90 eV. We are encouraged to feel that this correction is valid since the As $2p$ spin-orbit splitting is brought closer to the experimental value of 35.8 eV.

To extract the differential bivirtual correlation-energy contribution (rows 1—8 in Table II) from the ground-state results, it is necessary to recognize that the total bivirtual

TABLE III. Atomic and molecular $2p$ BE's for P, As, and Se (eV).

Level	DS[a]	Atom DF[b]	DF+Corr[d]	Molecule expt.
P $2p_{1/2}$	139.58	139.71	140.70	137.2(2)[e]
P $2p_{3/2}$	138.00	138.13[c]	139.12	136.2(2)[e]
As $2p_{1/2}$	1368.04	1368.18	1368.89	1365.9(2)[f]
As $2p_{3/2}$	1331.98	1332.12[c]	1332.83	1330.1(2)[f]
Se $2p_{1/2}$	1483.82	1484.16	1484.88	
Se $2p_{3/2}$	1442.69	1443.03[c]	1443.75	1441.4(2)[f]

[a] DS Δ SCF results from Ref. 11.

[b] DF Δ SCF results using the program described in Ref. 10.

[c] Obtained by increasing the $2p_{3/2}$ DS value in column 2 by the difference between the DF and DS values for $2p_{1/2}$. The $2p_{3/2}$ BE would be 1332.98 and 1443.90 eV for As and Se, respectively, if a 0.15-eV added correction is applied to the DF-DS values. The 0.15 eV is obtained from the Zn $2p$ BE in Ref. 12.

[d] Obtained by adding the computed correlation energies (Table II) to the values in column 3.

[e] From Refs. 27 and 30.

[f] This work.

energy $E_{vv'}$ to first order is given by the expression[21]

$$E_{vv'}=\sum_{k} C_k^2 \sum_{\substack{k_a,k_b \\ k_a \le k_b}} \sum_{S,L} T^2_{k_a k_b;SL}\,\epsilon(n^a l^a, n^b l^b; S,L) + \sum_{\substack{k,l \\ k\neq l}} C_k C_l (-1)^{m_{kl}} \sum_{S,L} T_{k_\alpha k_\beta;SL} T_{l_\alpha l_\beta;SL} \times \epsilon(n^\alpha l^\alpha, n^\beta l^\beta; S,L)\ . \qquad (4)$$

The HF function Φ is given by

$$\Phi=\sum_k C_k \Delta_k \qquad (5)$$

and in (4), k_a and k_b are the spin orbitals belonging to the HF determinant Δ_k associated with subshells $n^a l^a$ and $n^b l^b$ which have been replaced by two virtuals. The second term arises from the interaction of two HF determinants which differ in only two spin orbitals (k_α, k_β of Δ_k and l_α, l_β of Δ_l), which have their $N-2$ common spin orbitals aligned, producing the phase factor $(-1)^{m_{kl}}$. The ϵ are called symmetry-adapted—pair energies and are assumed to be invariant from state to state (in essence, they correspond to the correlation energies of a He atom with the indicated configuration and term), so all we must do is find their coefficients in the various states.

In earlier work,[5] we have given an explicit expression for the T's, viz.,

$$T_{k_a k_b;SL}=(-1)^{l^a+l^b+M_L+M_S}\left[\frac{(2S+1)(2L+1)}{N}\right]^{1/2} \times \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & S \\ m_s^a & m_s^b & -M_s \end{pmatrix} \begin{pmatrix} l^a & l^b & L \\ m^a & m^b & -M_L \end{pmatrix}, \qquad (6)$$

where $N=2$ if the subshells a and b are equivalent, and $N=1$ otherwise. While several special cases can be explicitly worked out,[5] we have designed a computer code[22] to evaluate the expression for an arbitrary case. To illustrate the procedure, for the ground state ($^4S^o$) of P, there are $\frac{1}{2}\epsilon\, 2p\,3p\ ^1S$ pairs, and in the hole state ^{5}P $\frac{1}{3}$ such pairs, so that the difference ($\frac{1}{6}$) is obtained by multiplying the ground-state $2p\,3p\ ^1S$ energy by $\frac{1}{3}$, which can be conveniently done as the program[20] automatically expresses energy contributions in symmetry-adapted form, whenever possible.

Table II also includes a contribution (-0.04 eV, assumed the same for both As and Se) from the final-state correlation $3d^2 \rightarrow 2p\,\epsilon f$ (as this dominates final-state correlation when it is an in-shell,[3] or SEOS, effect, e.g., $3d^2 \rightarrow 3p\epsilon f$, it is likely the largest off-shell effect of the type $3l3l' \rightarrow 2p\epsilon l''$). Since the hole state lies about 44.5 a.u. *above* the threshold (in As) for the process, we must compute the correlation (energy shift) by other means. Here we use a method[6] based on the work of Fano[7] and Altick,[8] where the shifted energy E is found by solving the transcendental equation

$$E-E_0=\mathscr{P} V \sum_k \int_{T_k}^{\infty} d\epsilon \frac{|V_{k\epsilon}|^2}{(E-\epsilon)}\ , \qquad (7)$$

where the hole-state energy is E_0, and the summation over k allows for different channels, each with their own threshold T_k. Now because the shift is small several approximations can be made which have no effect (to the desired accuracy). These include (1) representing the hole state and the continuum with HF functions, which in the latter case were computed with the frozen-core program of Bates,[23] (2) assuming the thresholds (three for $3d^2 \rightarrow 2p\epsilon f$) are independent of the channel, which allows the sum over k to be immediately performed. One finds that it is the same regardless of the coupling scheme, a result underlying the simplicity of Eq. (4) as well, and hence the scheme may be chosen to reduce interchannel coupling, which is obviously not present in Eq. (7), and finally (3) replacing E by E_0 on the right-hand side of the equation.

Wave functions from $\epsilon=0$ to 90.0 a.u. were generated from the Bates[23] program, after it was suitably redimensioned, $V_{k\epsilon}$ computed, and the integration performed numerically over this range. The higher $V_{k\epsilon}$ were then fit with a function of the form $1/\epsilon^{\alpha}$, to avoid the difficulty of directly constructing functions of even higher energies, and the remaining part of the integral (in practice up to 1500 a.u.), also evaluated numerically. The resulting shift was -0.038 eV, and has been included in Table II.

Some comments on the behavior of $|V_{k\epsilon}|^2$ as a function of ϵ are in order. Superimposed on the background which slowly reached a peak at $\epsilon=10.00$ a.u. and then slowly declined, were a series of "blips" at $\epsilon=2.4$, 2.5, 44.6, 48.0, 65.0, and 100.0 a.u. which were very narrow (10^{-3} a.u.) and differed in strength from the background by as much as an order of magnitude. Although due to their small width they had negligible effect on the shift, the extreme narrowness indicates that many more such blips are possible. The blips do not seem directly connected with the Cooper minima observed in photoionization cross sections,[24,25] as they are more frequent, do not just appear at "low" energies, and involve nodeless radial functions. It may be that they are a resonance phenomenon in which the wavelength of the electron matches the dimensions of the ionic "well."

III. EXPERIMENTAL METHOD AND RESULTS

The binding energies were measured by gas-phase XPS using Al*Kα* radiation (1486.582 eV).[26a] The spectrometer is located at Vanderbilt University and is designed specifically for high-temperature XPS work. Solid As and Se samples were heated (~300 °C for As and ~240 °C for Se) until sufficient vapor pressure was obtained for recording the $2p$ spectra. To our knowledge, no $2p$ level has ever been studied by gas-phase XPS in species containing As or Se.[27] For As it was possible to measure both the $2p_{1/2}$ and $2p_{3/2}$ binding energies and the spectra are shown in Fig. 1. For Se, the $2p_{1/2}$ binding energy is only a few eV less than the energy of the exciting radiation (Al*Kα*) and as a result the background from low-energy electrons precluded the study of this level. Even for the $2p_{3/2}$ level (Fig. 2), a high sloping background was observed, since the kinetic energy of the photoelectrons is only ~50 eV. However, it was still possible to measure the peak with good statistics due to the high photoionization cross section.[28] For both As and Se, the vapor is molecular rather than atomic. Under the conditions of our experiment, arsenic is expected to vaporize as As_4, while the selenium vapor is probably predominantly Se_5 and Se_6, with small amounts of Se_7 and Se_2.[29] That one or two species with nearly equal number of atoms are dominant can be seen from the fact that a relatively narrow peak is obtained with the linewidth being only ~0.1 eV greater than that of the As $2p$ peaks.

To obtain absolute binding energies, argon was mixed with the high-temperature vapor and the $\mathrm{Ar}\,L_3M_{2,3}M_{2,3}\,{}^1D_2$ Auger line [203.49(5) eV][26b] was scanned alternately with the level under study. The binding energies thus obtained are given in column 5 of Table III. The P $2p$ BE in gaseous P_4 has been reported previously by Banna *et al.*[30] and is also given in Table III.

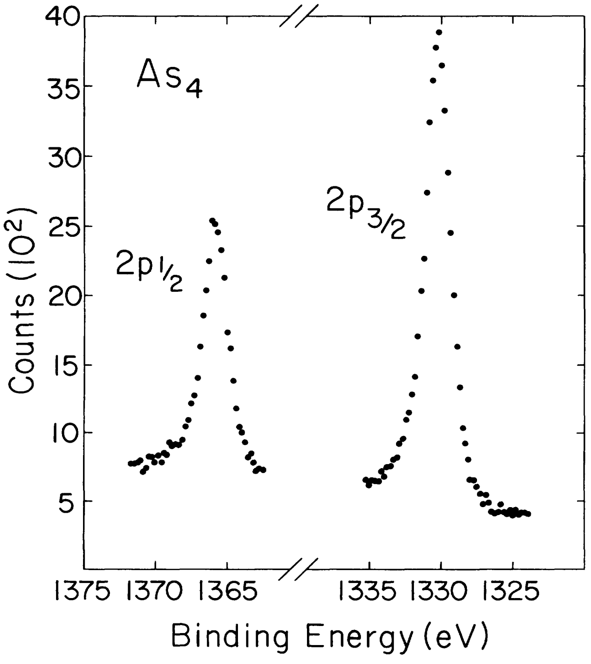

FIG. 1. As $2p$ levels in gaseous As_4 measured using 1486.6-eV x rays.

TABLE IV. Atomic $2p_{3/2}$ BE for As and Se (eV).

	DF+Corr[a]	Semiempirical[b]
As	1332.83	1332.2
Se	1443.75	1442.7

[a] From Table III.
[b] From Ref. 31.

IV. DISCUSSION

Our accurate atomic binding energies make it possible to test the validity of semiempirical methods used by other workers to determine these quantities. In Table IV we compare the results of Aksela *et al.*[31] with our many-body calculations (on As and Se $2p_{3/2}$). Although our $2p_{3/2}$ values are somewhat uncertain due to the use of corrected DS ΔSCF values rather than the more accurate DF, it is clear that the semiempirical binding energies are too low since our values are likely to be too low. Aksela *et al.* linearly interpolated the correlation energies of As and Se using the known $2p_{3/2}$ BE for Zn and Kr. However, there are now enough results available to suggest a correlation trend for the atomic $2p$ nonrelativistic correlation energy. In earlier work[3] it was found that the correlation energy for K is 0.7 eV, and by subtracting the DF value from the measured[32] Zn $2p_{3/2}$ BE, we find the correlation correction to be a similar number, viz., 0.6 eV. For both K and Zn, the correction to the DF value is nearly independent of j, offering additional indirect evidence of the validity of the approximations made earlier. Combined with the results of Table II this suggests that at least for systems where the $2p$ hole is not "near" the valence shell (as it is in P), the nonrelativistic correlation energy is nearly constant, ~0.7 eV. This is contrary to the behavior suggested by Aksela *et al.*,[31] where the $2p$ correlation energy rapidly decreases with Z, even undergoing a sign change at Se. The discrepancy could arise, for example, by the unwitting inclusion in that work of other, more Z dependent, effects

TABLE V. Atom-molecule BE shifts (eV).

Atom-Molecule	Level	atom-molecule Shift
Bi/Bi_2	$4f_{7/2}$	1.0[a]
I/I_2	$3d_{5/2}$	1.0[b]
F/F_2	1*s*	2.8[c]
Cl/Cl_2	1*s*	1.2[c]
Br/Br_2	1*s*	1.0[c]
Na/Na_3	1*s*	2.1[d]
P/P_4	$2p_{1/2}$	3.5[e]
As/As_4	$2p_{1/2}$	3.0[f]
Se/Se_n	$2p_{3/2}$	2.4[f]
Sb/Sb_4	$3d_{5/2}$	1.7,[g] 2.3[i]
Te/Te_2	$3d_{5/2}$	1.2,[h] 1.8[i]

[a] From Ref. 33.

[b] From Ref. 34.

[c] From Ref. 35.

[d] From R. L. Martin, E. R. Davidson, M. S. Banna, D. C. Frost, C. A. McDowell, and B. Wallbank, J. Chem. Phys. 68, 5006 (1978).

[e] From Ref. 30 and the atomic results obtained in this work.

[f] This work.

[g] From Ref. 36.

[h] From Ref. 37.

[i] Semiempirical atomic binding energies obtained from Ref. 31. Molecular binding energies for Sb_4 from Ref. 36 and for Te_2 from Ref. 37.

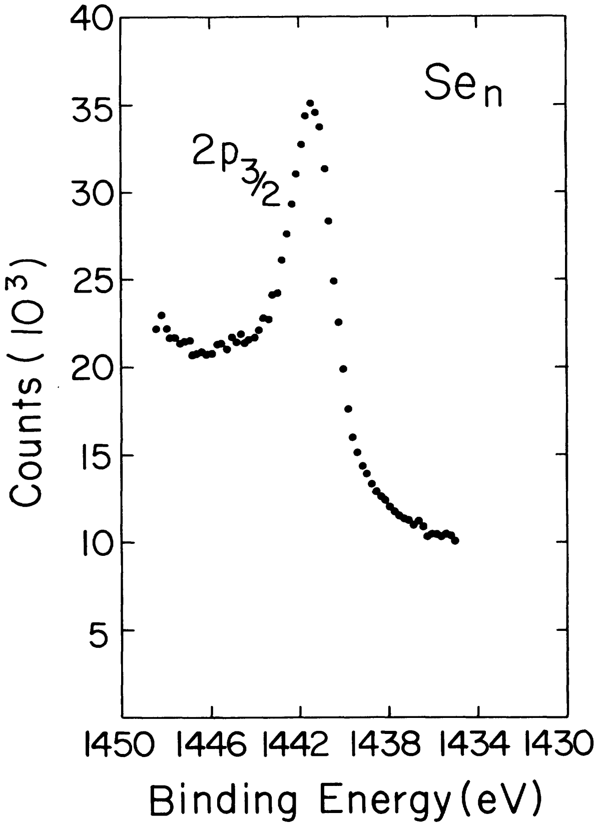

FIG. 2. Se $2p_{3/2}$ level in gaseous $Se_{5,6}$ measured using 1486.6-eV x rays.

(including those arising from exchange or relativistic correlation). Given the complexity of the problem as exhibited by the cancellation of large contributions in Table II which already had much cancellation removed *a priori*, it does seem clear that "simple rules" are not going to stand the test of time in this developing field.

Turning to molecular binding energies, in Table V we show a number of experimental as well as theoretical binding energies of both atoms and homonuclear molecules. In general, it is difficult to carry out measurements on both atomic and molecular species. Among the few systems in which this has been done are Bi/Bi_2 (Ref. 33) and I/I_2.[34] In some instances, the atom-molecule *shift* is quite reliable, such as for F/F_2, Cl/Cl_2, and Br/Br_2 since the calculations performed by Martin and Davidson[35] are quite accurate. For Sb and Te, molecular binding energies have been determined by Banna *et al.*,[36,37] but the atomic values are from DF calculations which do not include correlation.[36] Semiempirical values have been obtained by Aksela *et al.*,[31] however, and are included in Table V.

Despite the varying degree of reliability of the values given in Table V, the trend is clear. In each case, the molecular binding energy is lower than the atomic binding energy. Although detailed molecular calculations are lacking for many of the systems in Table V, it is likely that extra-atomic relaxation is in part responsible. It arises from the charge distribution on atoms neighboring the ionized center. The calculations of Martin and Davidson,[35] for example, show that for the halogens, the molecular binding energies would have been higher than the corresponding atomic values had it not been for extra-atomic relaxation. In general, the results in Table V suggest that as far as their effect on binding energies, relaxation, which is of course a final-state effect, seems to dominate over ground-state effects such as charge withdrawal due to bond formation, etc.

The atom-molecule shifts in P, As, and Se show an interesting trend. The Se/$Se_{5,6}$ shift is the smallest of the three. This at first appears unusual since extra-atomic relaxation should increase with cluster size and therefore the shift in Se would be expected to be larger than in P and As where the molecules are tetra-atomic. However, the number of atoms bonded to the ionized atom also plays a role, and it is therefore not surprising that the shift is larger in As than in Se, since in As each atom is bonded to three others while in Se each is bonded to two others. The semiempirical shift in Se of 2.4 eV is perhaps slightly lower than the true value given that the corrected DS results used to obtain the $2p_{3/2}$ atomic binding energy are probably somewhat low, as discussed above.

The P/P_4 shift is the largest of the three, despite the higher polarizability of As and Se. One possible explanation is that extra-atomic relaxation is larger than in As_4 due to the shorter bond lengths in P_4 compared to As_4. Martin and Davidson[35] observed a similar behavior in the diatomic halogens. An additional factor may be the smaller ground-state shift (in the direction of higher binding energy for the molecule compared to the atom) in P_4 than in As_4 and $Se_{5,6}$ due to the P 2*p* level being considerably shallower than the As 2*p* and Se 2*p* levels.

In Table VI the atomic As and Se 2*p* BE are compared with the corresponding BE in the molecules and in the

TABLE VI. As and Se $2p_{3/2}$ BE (eV).

Atom[a]	Molecule[a]	Solid[b]
As 1332.83	1330.1	1328.7[c]
Se 1443.75	1441.4	1438.6[d]

[a] From Table III.

[b] From Ref. 38.

[c] Using a work function of 5.1 eV from Ref. 38.

[d] Using a work function of 4.7 eV from Ref. 38.

solids.[38] For these two elements in the solid state, the available BE are not very accurate. For example, the spin-orbit splitting in As $2p$ disagrees with our reliable gas-phase measurement (35.5 eV vs 35.8 eV in the gas phase). Still, the expected trend of lower binding energy can be seen from the approximate values. Again, extra-atomic relaxation is probably an important contributor to the shift. This is probably the main reason for the molecule-solid shift being $\sim$1.4 eV in As while it is twice as much in Se, since in As most of the extra-atomic relaxation has already been realized in the molecule.

In conclusion, this work shows the feasibility of studying homonuclear species other than diatomics by gas-phase XPS. In this respect it complements studies of supported clusters which have received considerable attention recently.[39] Our work also shows that it is possible to calculate atomic binding energies with high accuracy for use in obtaining atom-molecule shifts for elements where the atomic species are difficult to study experimentally with currently available instrumentation.

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