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Orbital-Based Interpretation of Electron Density Differences in Ne_2 and Polarized Ne and Ne^{6+}

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Total and orbital density difference contours have been calculated from Hartree−Fock wave functions (uncontracted 14s9p4d3f basis) for three systems: Ne and Ne^{6+} polarized by a +1 charge at 4.66 bohr and Ne_2 ($R = 3.80$ bohr). Effects of MP2 correlation corrections are found to be negligible. In Ne, the outer portion of every orbital is polarized toward the +1 charge. The hybrid [2s + (0.0096)$2p_z$] is an excellent approximation to this system's 2s orbital, whose density difference reverses polarity within its circular node. Farther out, a large intermediate region of the 2pσ orbital is also polarized away from the +1 charge. In Ne_2, only 1s and 2s densities show dipolar polarization: the 2s toward the other nucleus due to 2pσ electron depletion in the atom-overlap region; the 1s in the opposite direction due to the 2s field. The latter effect is also observed in polarized Ne^{6+}. The total Ne_2 density difference exhibits atomic quadrupolar polarization due to unpolarized 2pσ density buildup and 2pπ depletion.

Introduction

Overlap of closed-shell atoms causes changes in their electron densities. Compared to the sum of the unperturbed atomic densities, the calculated density in He_2 decreases in the overlap region and increases both close to and beyond the nuclei.[1,2] These changes are accompanied by a new feature in Ne_2 and Ar_2.[3] A cylindrically symmetric layer of density decrease extends outward from each nucleus. This torus extends continuously through the internuclear axis of Ne_2. In Ar_2 it does not reach the axis, though much smaller disconnected regions of density decrease cross the axis on both sides of each nucleus. Consequently, the sign of the density difference along the axis changes sign six times in Ne_2 and 10 times in Ar_2.

The density changes in He_2 are easily explained. The decrease in the overlap region results from Pauli repulsion between electrons with the same spin. The increases elsewhere result from conservation of electrons and from their attraction to the nuclei. Less obvious is the cause of the additional density decrease that is common to Ne_2 and Ar_2. Its explanation is one goal of this investigation.

We also examine density differences in a neon atom due to polarization by a nearby positive point charge. Density-difference contours due to uniform electric fields have been previously calculated for HF,[4,5] F_2,[6] and Ne.[7] These density differences reverse sign repeatedly in the electric field direction. Feil[7] used second-order perturbation theory to explain the number of sign reversals in Ne. Another goal of our investigation is to provide additional explanations for the complicated pattern of density differences in polarized Ne.

The point-charge-polarized neon atom serves as a model for a multishell noble gas atom near a cation. This model incorporates the dominant feature of the atom−ion electrostatic interaction without complication by interatomic Pauli repulsion. The Ne_2 system serves as a model for the Pauli repulsion interaction between overlapping closed-shell multishell atoms such as atomic ions or noble gas atoms. The polarized Ne^{6+} ion enables us to test our explanation for a surprising feature of the 1s density difference in Ne_2.

Calculations

For Ne and Ne^{6+} polarized by a +1 point charge, the point charge was placed at 4.66 bohr, the equilibrium internuclear distance R_e of $NeNa^+$.[8] The internuclear distance of Ne_2 was chosen as 3.80 bohr so that the effects of compression on electron density would be markedly greater than would be observed at R_e, 5.84 bohr.[9]

Wave functions were calculated in the Hartree−Fock and Møller−Plesset MP2 approximations by Gaussian 94.[10] The Gaussian atomic basis set for all systems consisted of the uncontracted 14s9p4d3f primitives from the ANO-L Ne basis set.[11] The exponential coefficients were obtained from the Molcas basis set library.[12]

Results

All figures are based on Hartree−Fock calculations. Figure 1 for a neon atom polarized by a +1 point charge and Figure 2 for Ne_2 include density difference maps for total density, the 2p subshell, and individual orbitals. Each difference is the specified density minus the corresponding density of the unpolarized atom(s). Even for Ne_2, the orbitals under consideration are distorted atomic orbitals, not molecular orbitals. The Ne_2 2s density difference, for example, is the two-atom composite of the changes in 2s AO densities. This difference is calculated as the sum of the 2sσ and 2sσ* MO densities minus the two undistorted 2s AO densities. MO and AO densities are for doubly occupied orbitals.

Ne Polarized by +1 Charge. The 1s density difference for this system (Figure 1f) has the expected dipolar character associated with a shift of electron density toward the positive external charge. The polarization is very slight, however. At the position of the maximum density difference, the polarized density is larger than the unpolarized by only 0.008%.

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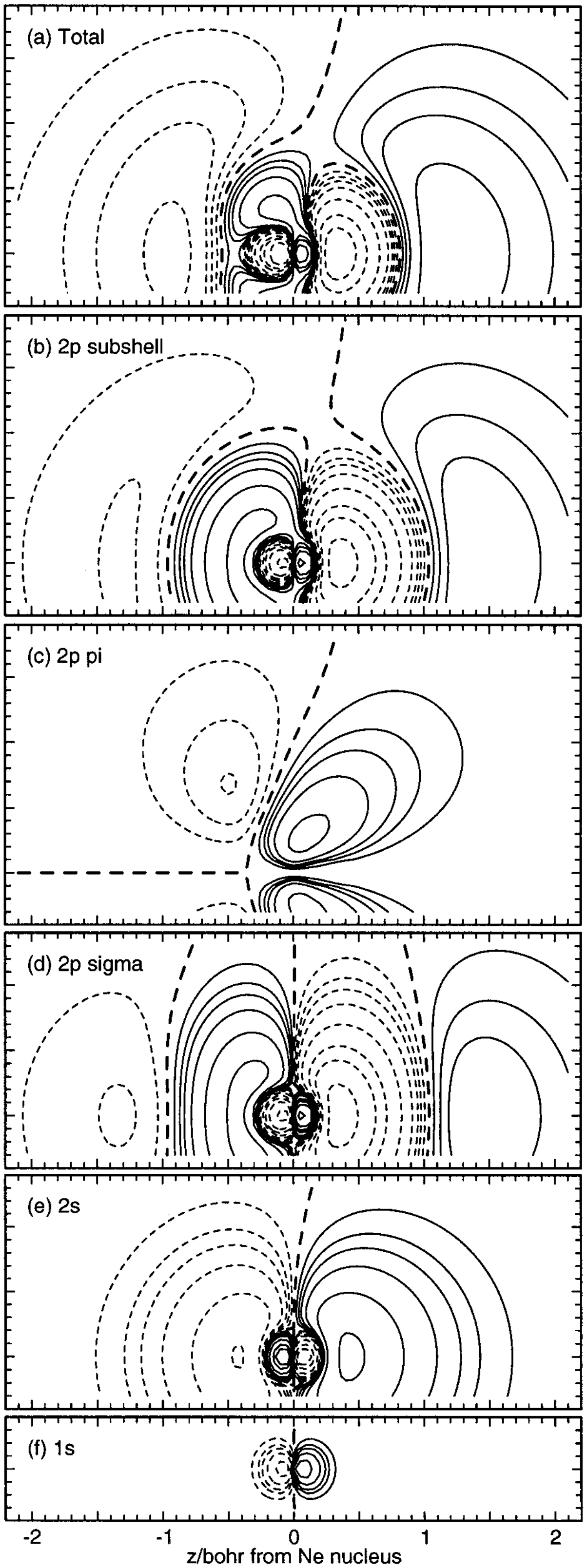

Figure 1. Density difference contours for a neon atom polarized by a +1 point charge. The nucleus is at the origin; the +1 charge is on the *z* axis at +4.66 bohr. Orbitals are doubly occupied. Positive contours are solid, negative ones are dashed, and zero contours are thick and dashed. The outermost contours are for differences of ±0.001 electrons $bohr^{-3}$. Successive ones are ±0.002, 0.003, 0.005, 0.01, 0.02, 0.03, 0.05, and 0.1 au.

The 2s density difference has an approximately spherical nodal surface that virtually coincides with the spherical node of the unpolarized 2s orbital. Outside this sphere, the density increases on the side toward the external charge and decreases not quite antisymmetrically on the opposite side. The density difference is also nearly antisymmetric inside the sphere, but there the polarization is in the opposite direction from that predicted by classical electrostatics.

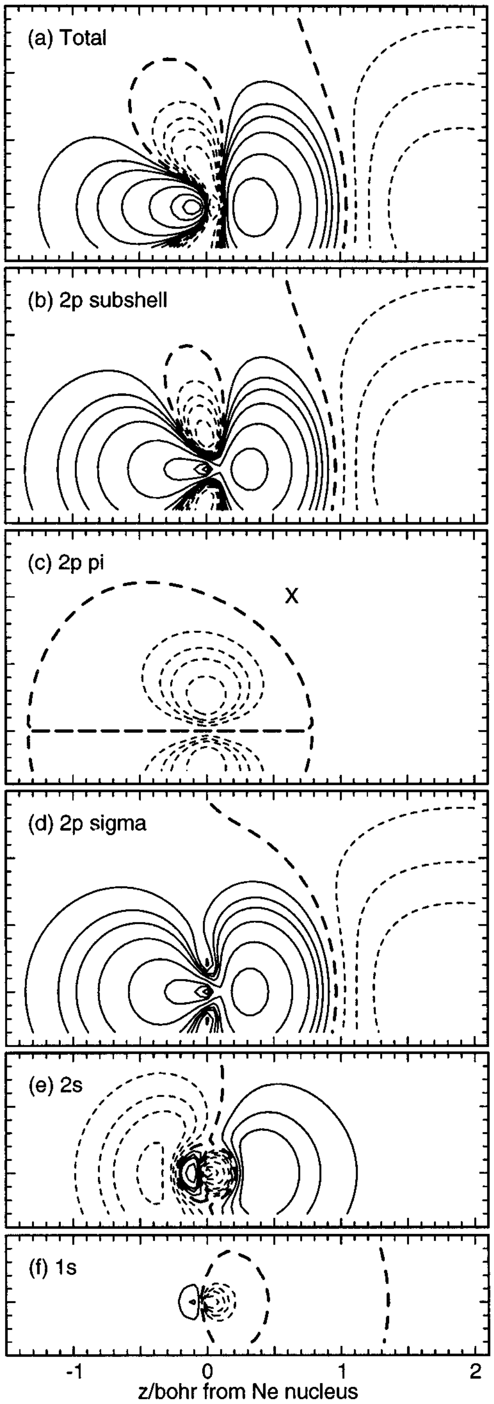

Figure 2. Density difference contours for Ne_2. Both neon nuclei are on the *z* axis, one at the origin, the other at +3.80 bohr. Densities for undistorted atoms at both sites have been subtracted from the corresponding Ne_2 density. Contour values are as in Figure 1.

Figure 3 of 2s and 2pσ densities along the *z* axis shows that the high-density portions of the 2pσ orbital are displaced *away* from the external positive charge. The peak value of the positive-*z* wing of the polarized 2pσ density is 2% less than that of the unpolarized density, but polarization scarcely affects the peak value of the negative-*z* wing. Only in regions more than 1.0 bohr from the nucleus is the 2pσ electron cloud

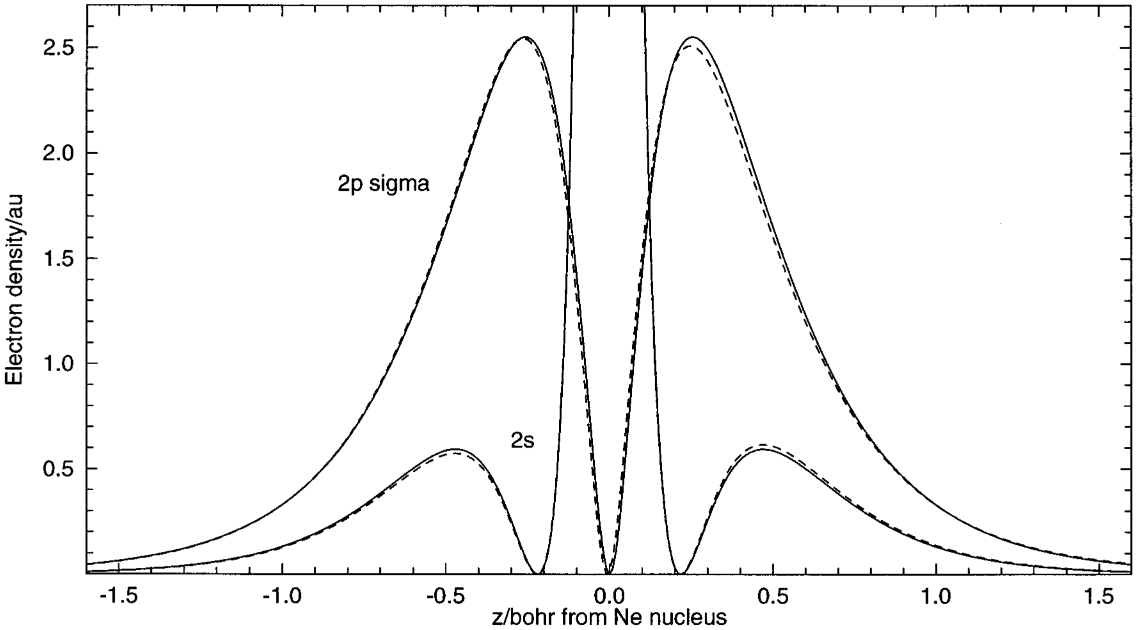

Figure 3. Polarized (dashed line) and unpolarized (solid line) neon 2s and 2pσ densities along the z axis. Polarization is by a +1 point charge at z = 4.66 bohr.

polarized in the direction predicted by classical electrostatics. In contrast, the outer wings of the 2s density are not displaced perceptibly in either direction. The classically expected 2s polarization results from a roughly 4% increase of density in the positive-z wing outside the spherical node and a roughly 4% decrease in the negative-z wing.

The 2pπ density difference (Figure 1c) is polarized in the general direction of the external positive charge, but also toward the z axis. (This density difference is zero everywhere along the z axis, despite the contour generator's failure to show this.)

Ne_2. The 2s and 1s density differences are less polarized for Ne_2 (parts e and f of Figure 2) than for the neon atom polarized by a +1 charge. The 2s orbitals for these two systems are polarized in the same direction and are qualitatively similar, including the polarization reversal close to the nucleus. The 1s orbitals, however, are polarized in opposite directions from each other.

The only atomic orbitals whose densities change appreciably as a direct consequence of atomic overlap are the 2pσ. Their combined density difference is negative throughout the central half of the internuclear axis. The 2pσ and 2pπ orbitals of Ne_2 are essentially unpolarized, quite unlike the corresponding orbitals of the point-charge-polarized atom. Instead, the largest-density region of the Ne_2 2pσ orbital is increased almost symmetrically, and that of the 2pπ is symmetrically decreased. The extremely diffuse density increase of the 2pπ orbital is shifted slightly toward the other atom. Positive 2pπ difference contours do not appear in Figure 2c because all are smaller than the 0.001 au threshold, but the X in this figure locates the maximum density difference. Its value is only 0.0003 au.

Gaussian 94 reports grids of orbital amplitudes to six significant figures. The resulting fractional errors in density differences are too small to affect noticeably any contours except possibly those in Figure 2f for the 1s orbital of Ne_2. Even in this case, the errors are too small to affect the direction of polarization.

Ne^{6+} Polarized by +1 Charge. Figure 4 consists of density difference maps for both occupied orbitals of this system. The 1s density difference contours are almost indistinguishable from those in the corresponding Ne system, except that the signs are reversed. The 2s density is polarized more strongly in Ne^{6+} than in Ne. The magnitudes of the outer extrema of the 2s density difference are over twice as large in Ne^{6+} as in Ne.

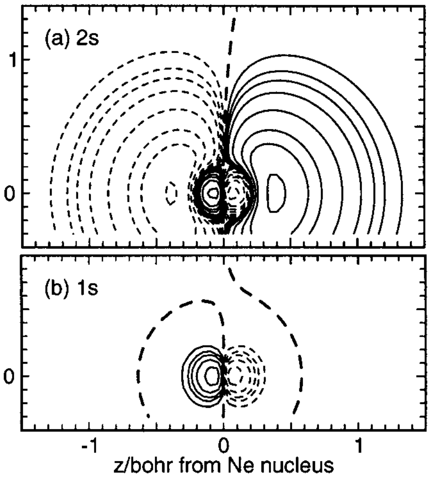

Figure 4. Density difference contours for orbitals of a Ne^{6+} ion polarized by a +1 point charge. The nucleus is at the origin; the +1 charge is on the z axis at +4.66 bohr. Contour values are as in Figure 1.

Effects of Electron Correlation. Although individual orbitals are strictly identical in the MP2 and Hartree–Fock approximations, the MP2 correlation correction does cause barely noticeable changes in the contours for total density difference.

In point-charge-polarized Ne and Ne^{6+}, these changes are imperceptible (at the scale of the figures) except in the outermost lobes. In polarized Ne, MP2 enhances the density increase in the lobe toward the external charge and enhances the depletion in the opposite lobe. In polarized Ne^{6+}, MP2 has the opposite effect, reducing the magnitudes of both the density increase and the depletion. The MP2 effects on Ne_2 contours are not easily summarized.

MP2 displaces even the outermost contours by no more than 0.09, 0.02, and 0.05 bohr for Ne, Ne^{6+}, and Ne_2, respectively.

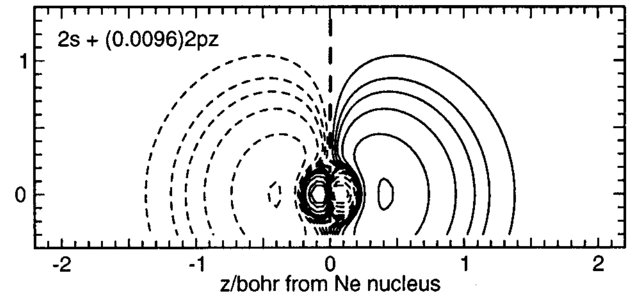

Figure 5. Density difference contours for normalized hybrid orbital [2s + (0.0096)2p$_z$] minus the 2s orbital. Orbitals are doubly occupied. The 2s and 2p$_z$ orbitals are those of the unpolarized neon atom. The 2s amplitude is negative at the nucleus. Contour values are as in Figure 1.

Discussion

Figures 1 and 2 show that, in both systems, the density difference of the 2p subshell has most of the qualitative features of the total density difference. One reason is that the nucleus holds 2p electrons less tightly than 2s or 1s. The 2p orbitals are therefore more susceptible to disturbances by an external charge or a second atom. In addition, only the two 2pσ orbitals overlap significantly in the diatomic system. A third reason applies solely to the atom polarized by an external charge. In this system, the density differences within the nearly spherical node of the distorted 2s orbital are offset to a considerable extent by the oppositely polarized 1s differences. In Ne$_2$, however, the corresponding differences reinforce each other. These negative differences cause the belt of negative density difference near the nucleus to cross the z axis for the total density difference even though it does not cross that axis for the 2p subshell density difference.

Ne Polarized by +1 Charge. The total density difference for this system (Figure 1a) is very complicated. The difference changes sign five times along the z axis, the electric field line that passes through the Ne nucleus. Feil[7] also obtained this result with Hartree−Fock−Slater calculations. The same number of sign changes in the field direction through the F nucleus (and possibly two more changes in F$_2$[13]) have been reported for HF[4] and F$_2$[6] subjected to a uniform electric field perpendicular to the internuclear axis.

The 2s orbital is more polarized than the 1s for several reasons. The 2s electrons are freer to respond to an external charge because they are farther from the nucleus and are screened from it by the 1s electrons. In addition, the polarized 2s orbital subjects the 1s electrons to a field that partly offsets the field from the external charge.

A surprising feature of the 2pσ and 2s differences is the region of reversed polarity close to the nucleus. This feature can be simulated by a slight hybridization between 2s and 2p orbitals of the unpolarized neon atom. The normalized hybrid orbital is

$$(1 + c^2)^{-1/2}[2s + c2p_z]$$

Figure 5, the hybrid's density difference map with $c = 0.0096$, is a good replica of Figure 1e, the corresponding difference map for the 2s orbital of the polarized atom.

The scale of these figures does not do justice to the hybrid orbital's excellent replication of nodes and extrema of the 2s density difference. For the polarized atom and for hybrids with c values of 0.0089 or 0.0096, the nearly spherical node of the 2s density difference intercepts the z axis at −0.220 and +0.218 bohr. These values match almost exactly the radius (0.218 bohr) of the node in the unpolarized 2s density (not difference). The z intercept of the difference node closest to the nucleus is −0.001 bohr for the polarized orbital and −0.002 bohr for both hybrids.

TABLE 1: Extrema of 2s Density Differences in Order of Increasing *z*

orbital	c	density differences (in electron bohr^{-3})			
polarized		−0.0205	0.0460	−0.0467	0.0221
hybrid	0.0089	−0.0191	0.0457	−0.0470	0.0193
hybrid	0.0096	−0.0205	0.0492	−0.0508	0.0208

Table 1 reports the extreme values of the density difference for the polarized 2s orbital and for hybrid orbitals with two values of the mixing coefficient c. The c value 0.0089 gives better approximations to the extrema within the nearly spherical node, whereas 0.0096 gives better values for the outer extrema. With either c, however, all four values are excellent, especially since the extrema are values of differences between much larger density values (Figure 3).

A hybrid orbital of the form [2p$_z$ − c2s] gives rise to a density difference function (relative to unpolarized 2p$_z$) that is the exact negative of the density difference of [2s + c2p$_z$] relative to 2s. (This surprising result is easily proved by showing that the sum of the two difference functions equals zero.) Thus, [2p$_z$ − (0.0096)2s] results in difference contours that are identical (except for sign) to those in Figure 5. Close to the nucleus, this hybrid simulates approximately the polarization of of the 2pσ orbital of the polarized atom (Figure 1d). Everywhere else, it is polarized *away* from the +1 charge. The more complicated pattern of Figure 1d has additional sign reversals. Feil's perturbation treatment[7] can provide a rationale for these outer reversals and for the inner ones as well.

Feil[7] used second-order perturbation theory to explain the occurrence of five sign reversals in the total density difference of a polarized Ne atom. He pointed out that this density difference is approximately proportional to the product of the unperturbed 2p$_z$ and 3s amplitude functions, i.e., the highest occupied orbital and the lowest unoccupied orbital that have the same symmetry under the applied external field. A straightforward extension of his argument to the density difference of the 2pσ orbital would give the same number of sign changes. This correct number would be preserved even if the resulting hybrid orbital involved 2s in addition to 3s contributions, since the radius of the 2s node is close to that of the inner 3s node.

Analogous mixing of 2pπ and 3pπ orbitals cannot replicate the density differences of the polarized 2pπ orbital (Figure 1c), presumably because of the larger difference between the orbital energies. Such mixing may, however, be responsible for the pronounced density shift toward the z axis, not just toward the external positive charge.

The complicated pattern of 2pσ density differences consists of one polarization within 0.2 bohr of the nucleus, an opposite polarization out to $z = \pm 1.0$ bohr, and an outermost polarization in the same direction as the innermost. Though the polarizations within 1.0 bohr are in opposite directions, both are due to the same slight displacements (Figure 3) of the high-density portions of the orbital. Because these shifts are away from the external positive charge, they raise the electrostatic interaction energy between the 2pσ charge distribution and the external charge. What causes shifts in this surprising direction? A lowering of interorbital energy may be responsible. Note (Figure 1) that, everywhere within 1.0 bohr of the nucleus, the 2pσ density difference and the 2s difference have opposite signs. Changes in the 2s density appear to be causing the shifts of the 2pσ orbital's high-density regions. The outer 2s maxima do not shift at all.

Ne_2. Pauli repulsion reduces the electron density of the Ne_2 2pσ atomic orbitals throughout an extensive overlap region (Figure 2d). This repulsion might have been expected to shift electron density primarily to the far side of each atom, resulting in dipolar polarization. Instead, the 2pσ density increases to similar extents in both lobes of the original $2p_z$ orbital. Surprisingly, the largest increase is at the nucleus, in what was the nodal plane of the original orbital. Therefore, the 2pσ orbital of Ne_2 must have some s character even though its density difference map lacks the opposing dipolar polarizations of the other system's slightly hybridized 2pσ orbital.

The density increase of the 2pσ orbital crowds the 2pπ orbital, most of which consequently undergoes a density decrease. The major portion of this decrease is remarkably symmetric. The compensatory density increase of the 2pπ orbital is extremely diffuse and is shifted toward the other atom. The X in Figure 2c locates the maximum 2pπ density difference.

The 2pσ density increase and the 2pπ decrease are together responsible for the patterns of density difference that originate near the nucleus in parts a and b of Figure 2. These patterns—positive differences in both directions along the *z* axis, but negative differences off axis—constitute atomic quadrupolar polarization. The layer of negative total density difference extends through the *z* axis because of the negative 1s and 2s density differences just to the right of the nucleus.

This quadrupolar pattern of the total difference, including crossing of the axis, persists in Ne_2 at internuclear distances of 2.5 and 4.0 bohr.[3] Ar_2 (at 4.0 bohr) has a similar quadrupolar pattern,[3] but its main region of density decrease does not reach the axis. Separate, much smaller negative regions do cross the axis on both sides of each Ar nucleus.

The 2s polarization is dipolar, not quadrupolar (Figure 2e). Overlap repulsion has no effect on the 2s density difference. The 2s density is a small fraction of the 2pσ density in the overlap region (Figure 3).

We propose the following explanation for the direction of the outer 2s polarization. The other atom attracts the 2s electrons of the first atom because the second atom's nuclear charge is not fully screened by electrons. The descreening is due to the decrease of electron density in the overlap region of the 2pσ orbitals. The same explanation accounts for the shift toward the second atom by the diffuse density increase of the 2pπ orbital.

The 2s density difference patterns for Ne_2 and the point-charge-polarized neon atom are similar not only in the direction of polarization but in the presence and size of a reversed-polarity region close to the nucleus. Such a region also appears in the 2pσ density difference of the point-charge-polarized neon atom but is missing from the Ne_2 2pσ difference, which is not dipole polarized at all.

The 1s density of Ne_2 is polarized in the opposite direction from the outer 2s polarization. We attribute this to the electric field from the polarized 2s orbital on the same atom. In the 1s region, this field is evidently stronger than the opposing field from the partially descreened other nucleus. In the point-charge-polarized Ne system, however, the 1s and 2s orbitals are both polarized in the same direction by the external +1 charge. This charge must be much larger than the effective charge of the other nucleus in Ne_2. The evidence for this claim is the fact that the external charge causes a much larger polarization of the 2s orbital (compare Figures 1e and 2e) even though the external charge is farther away than the second nucleus.

Ne^{6+} Polarized by +1 Charge. Control of 1s polarization by 2s polarization is also observed in the polarized Ne^{6+} ion (Figure 4). The 2s density is polarized more strongly in Ne^{6+} than in Ne because 2s is the outermost orbital of Ne^{6+}. The 2s polarization in Ne^{6+} is strong enough to overwhelm, not just reduce, the effect of the external +1 charge on the 1s orbital. The zero contours in Figure 4b provide further support for this interpretation. Outside these contours, which cross the *z* axis at ±0.6 bohr, the 1s polarization reverts to the direction imposed directly by the +1 charge (i.e., positive density difference toward the +1 charge, negative difference away from it). Both these outer regions are beyond the outer extrema (at ±0.4 bohr) of the 2s density difference. Similarly, the zero contours in Figure 2f show that the 1s density difference of Ne_2 is positive between the maximum of the 2s density difference and the overlap region.

Summary

Simpler changes in orbital densities underlie the complicated changes in the total density of neon due to an external +1 point charge. As expected, at least the outer region of every orbital is dipole polarized toward the +1 charge. A very slight amount of sp hybridization causes the polarizations of the 2s and 2pσ orbitals to change sign across the 2s spherical node. At intermediate distances from the nucleus, the 2pσ orbital is polarized away from the external charge, apparently to diminish repulsive interactions with the 2s orbital.

The main features of the total density change in Ne_2 are quadrupolar polarization of each atom and density decrease in the overlap region between them. The latter decrease involves only the 2pσ orbitals. The compensatory 2pσ increase occurs almost symmetrically in the main region of this orbital. This increase crowds the 2pπ electrons and causes a symmetric density decrease in the main region of their orbital. The interrelated 2pσ increase and 2pπ decrease are responsible for the quadrupolar polarization. The density decrease in the overlap region exposes the 2s electrons to attraction by the other atom's nucleus. The resulting dipole polarization of the 2s orbital toward this nucleus polarizes the 1s orbital in the opposite direction.

Similarly, an external +1 point charge polarizes the 2s orbital so much more in Ne^{6+} than in Ne that the 1s orbital in Ne^{6+} (though not in Ne) is polarized away from the +1 charge.

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(13) Labeling of some contours in Figure 3a of ref 6 is inconsistent with the symmetry. In addition, the field directions in refs 4 and 6, unlike ref 5 and the present work, are inconsistent with the signs of density differences in the outer regions.