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Coulomb shifts for intra- and intershell electron pairs in LiH

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The influence of electron correlation on the interparticle momentum distribution $f(p_{12})$, where $p_{12} = |\mathbf{p}_1 - \mathbf{p}_2|$, is examined for the individual intra- and intershell electron pairs in LiH. These changes $\Delta f(p_{12})$ vs p_{12} , known as Coulomb shifts, are compared with a similar and earlier analysis of correlation effects in momentum space for the united-atom Be. Selected expectation values are also reported at both the correlated and Hartree-Fock levels of approximation. The use of momentum space for such a study is particularly advantageous for a molecule since, unlike an analysis in position space, the calculation is reduced in complexity by being effectively single-centered. Consequently, atomic-based concepts such as "radial" and "angular" correlation remain applicable. For this initial example of a many-electron molecule, the Coulomb shifts for LiH emphasized the ionic components of the two intrashells, as well as their reduced interdependence by comparison with Be. Correlation produced an increase in momentum, especially for the more loosely bound electrons. This corresponds to a contraction of the charge density in the outer regions of the molecule when viewed in position space.

I. INTRODUCTION

For a two-electron system, Coulson and Neilson¹ examined electron correlation in terms of a Coulomb hole $\Delta f(r_{12})$ vs r_{12} , defined as the difference between the correlated and Hartree-Fock (HF) distributions for the interparticle scalar separation $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. Subsequently, this concept was used to assess correlation effects in many-electron atoms: see, for example, the work on Be by Benesch and Smith² and Banyard and Mobbs³ and references therein. A complementary investigation can be made in momentum space⁴ by evaluating the analogous difference function $\Delta f(p_{12})$ vs p_{12} , where the scalar quantity $p_{12} = |\mathbf{p}_1 - \mathbf{p}_2|$. The Coulomb shift, as the momentum "hole" is called, has been analyzed for several ground-state atomic systems,⁴⁻⁶ including an in-depth study of Be by the present workers.⁷

For a molecule, the computation of a Coulomb hole is complicated due to the multicenter nature of the wave function. The difficulties which arise were summarized by Lester and Krauss⁸ in their study of H_3^+ . To ease the problem, they used a Gaussian basis set to determine correlated and non-correlated descriptions of the distribution function $f(r_{12})$ of the vector \mathbf{r}_{12} . Gaussian basis sets have also been used to examine correlation effects for H_2 , see Sharma and Thakkar.⁹ For a Slater basis set, although the use of a multicenter wave function to calculate an interparticle distribution function remains complex, Stewart¹⁰ has shown how such a function can be obtained by a Hankel transform from scattering intensities computed by the methods of Bentley and Stewart.^{11,12} For HeH^+ , Slater-type orbitals have been used in an extensive one-center $1\Sigma^+$ symmetry wave function¹³ to determine Coulomb holes, as defined by Coulson and Neilson,¹ and also various partial Coulomb holes at selected values of R the internuclear separation.¹⁴

The evaluation of a Coulomb shift for a molecule using

multicenter wave functions is, however, more straightforward since the transformation of the wave functions into momentum space makes the calculation effectively single-centered. Consequently, this feature coupled with the renewed interest in momentum space and related properties,¹⁵⁻²⁰ suggests that the Coulomb shift $\Delta f(p_{12})$ vs p_{12} should be effective when assessing correlation effects within molecules. Moreover, being single-centered, the atomic-based terminology "radial" and "angular" correlation remains useful. Therefore, as a first example of a many-electron molecule, Coulomb shifts are reported for LiH and, by applying a previously devised partitioning technique²¹ to the second-order density, correlation effects can be examined within the individual electronic shells. The choice of LiH allows comparisons to be made with the united-atom Be⁷; limited comparisons are also made with Li^+ and H^- .

II. CALCULATIONS AND RESULTS

Following the analysis of Be($1S$) in momentum space,⁷ the Coulomb shift associated with a pair of occupied HF molecular spin-orbitals ϕ_i and ϕ_j in momentum space can be written as

$$\Delta f_{ij}(p_{12}) = \int \Delta \Gamma_{ij}(\mathbf{p}_1, \mathbf{p}_2) d\mathbf{p}_1 d\mathbf{p}_2 / dp_{12}. \quad (1)$$

The integration applies to all space-spin coordinates of electrons 1 and 2 except for the interparticle momentum scalar separation $p_{12} = |\mathbf{p}_1 - \mathbf{p}_2|$. The change, due to correlation in the (i, j) component of the second-order density $\Delta \Gamma_{ij}(\mathbf{p}_1, \mathbf{p}_2)$, was obtained by applying the partitioning technique of Banyard and Mashat²¹ to the momentum representation of the correlated wave function; the restricted HF description in momentum space could be partitioned exactly. We note that each $f_{ij}(p_{12})$ is normalized to unity and the integral of $\Delta f_{ij}(p_{12})$ vs p_{12} is identically zero.

The internuclear separation for LiH is restricted to the experimental value of $R = 3.015$ a.u.²² and, because of the

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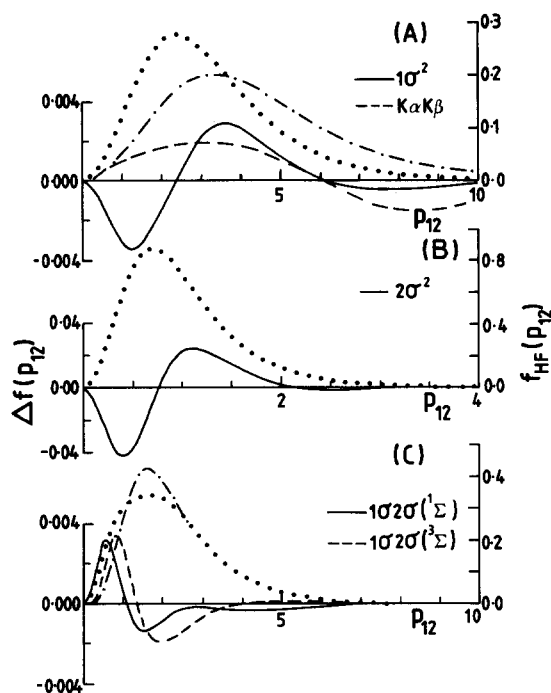


FIG. 1. Coulomb shifts $\Delta f(p_{12}) = f_{\text{corr}}(p_{12}) - f_{\text{HF}}(p_{12})$, for the intra- and intershell electron pairs in LiH: (A) $1\sigma^2$; (B) $2\sigma^2$; (C) $1\sigma 2\sigma(^1\Sigma)$ and $1\sigma 2\sigma(^3\Sigma)$. Shown in (A) for comparison are the $K\alpha K\beta$ results for Be(1S): --- $\Delta f(p_{12})$ and - - - $f_{\text{HF}}(p_{12})$. The $f_{\text{HF}}(p_{12})$ curves for $1\sigma^2$, $2\sigma^2$, and $1\sigma 2\sigma(^1\Sigma)$ are indicated by · · · in (A), (B), and (C), respectively. The $f_{\text{HF}}(p_{12})$ results for $1\sigma 2\sigma(^3\Sigma)$ are shown in (C) as - - - and become graphically indistinguishable from the $1\sigma 2\sigma(^1\Sigma)$ curve when $p_{12} > 2.5$.

convenience of its structure and its basis set, we use the correlated wave function of Arrighini *et al.*²³ This 262-term configuration-interaction (CI) wave function in position space for LiH($^1\Sigma$) is formed from a set of 19 orthonormal basis functions constructed for 11 Slater-type orbitals (STOs) centered on Li and 8 STOs centered on the H nucleus. The leading configuration is by design a good approximation to the restricted HF description, hence our analysis

was eased considerably by using it as the HF reference state. The correlation terms represent all possible single- and double-excitations from this HF reference state and as such, they recover in excess of 82% of the correlation energy. Arrighini *et al.*²³ made no allowance for triple and quadruple excitations. The momentum representation of this CI wave function, and its HF leading configuration, was obtained by applying the Dirac-Fourier transform procedure²⁴ to the STO basis set.

With (i, j) -pair selections of (1, 2) and (3, 4), Coulomb shifts were calculated for the two doubly occupied molecular intrashells $1\sigma^2(^1\Sigma)$ and $2\sigma^2(^1\Sigma)$, respectively. The results are shown in Figs. 1(A) and 1(B); Figure 1(A) also includes $\Delta f(p_{12})$ for the $K\alpha K\beta(^1S)$ shell in Be. For the inter-shell orbital pairs (1, 4) and (2, 3), expressions for $\Delta\Gamma_{ij}(p_1, p_2)$ were combined and rewritten to produce results appropriate to the singlet and triplet spin states $1\sigma 2\sigma(^1\Sigma)$ and $1\sigma 2\sigma(^3\Sigma)$; the Coulomb shifts are given in Fig. 1(C). For comparison, the corresponding molecular $f_{\text{HF}}(p_{12})$ distributions are also presented in Fig. 1. In Fig. 2 we show the normalized sum total Coulomb shift for LiH, defined as $\frac{1}{2}\sum_{i>j}^4 \Delta f_{ij}(p_{12})$, and the associated total $f_{\text{HF}}(p_{12})$ curve. In Table I we report selected one- and two-particle expectation values; also quoted is Υ —the percentage of each $f_{\text{HF}}(p_{12})$ probability density which has been redistributed due to electron correlation.

III. DISCUSSION

Figure 1(A) reveals a distinct difference between the Coulomb shifts for $1\sigma^2(^1\Sigma)$ in LiH and the $K\alpha K\beta(^1S)$ shell in isoelectronic Be; the difference is particularly noticeable when $0 < p_{12} < 3$. For 1S intrashell electron pairs, Banyard and Reed⁴ established that radial correlation produces a $\Delta f(p_{12})$ curve which is initially negative whereas, by contrast, angular correlation gives rise to a Coulomb shift which is positive at small p_{12} . Clearly, for the $1\sigma^2(^1\Sigma)$ shell in LiH, the wave function of Arrighini *et al.*²³ indicates that radial correlation is dominant. For the K shell in Be, the behavior

TABLE I. Intra- and intershell electron pair values for $\langle p_1^n \rangle$, $\langle p_{12}^n \rangle$, $\sigma(q)$, and Υ for the ground state of LiH when the internuclear separation $R = 3.015$ a.u. (Ref. 22).

Wave function	Shell	$\langle p_1^{-1} \rangle$	$\langle p_1^1 \rangle$	$\langle p_1^2 \rangle$	$\sigma(p_1)^a$	$\langle p_{12} \rangle$	$\langle p_{12}^2 \rangle$	$\sigma(p_{12})^a$	$\Upsilon\%$ ^b
CI ²³	$1\sigma^2(^1\Sigma)$	0.6591	2.2433	7.2151	1.4774	3.2838	14.2552	1.8633	0.596
	$2\sigma^2(^1\Sigma)$	2.1915	0.7082	0.7882	0.5354	1.0468	1.5443	0.6697	1.809
	$1\sigma 2\sigma(^1\Sigma)$	1.4253	1.4756	3.9997	1.3499	2.2880	7.1423	1.3811	0.185
	$1\sigma 2\sigma(^3\Sigma)$	1.4252	1.4758	4.0005	1.3500	2.4235	7.9279	1.4334	0.213
	Total ^c	1.4253	1.4758	4.0007	1.3501	2.3148	7.7876	1.5585	1.533
HF ²³	$1\sigma^2(^1\Sigma)$	0.6588	2.2432	7.2210	1.4762	3.2878	14.2120	1.8445	...
	$2\sigma^2(^1\Sigma)$	2.1825	0.7071	0.7813	0.5304	1.0624	1.5718	0.6656	...
	$1\sigma 2\sigma(^1\Sigma)$	1.4207	1.4752	3.9962	1.3491	2.2848	7.1352	1.3838	...
	$1\sigma 2\sigma(^3\Sigma)$	1.4207	1.4752	3.9962	1.3491	2.4222	7.9368	1.4387	...
	Total ^c	1.4207	1.4752	3.9962	1.3491	2.3169	7.7882	1.5556	...

^a $\sigma(q)$ is the standard deviation of the quantity q .

^b $\Upsilon\%$ is the percentage of the normalized $f_{\text{HF}}(p_{12})$ vs p_{12} function which has been redistributed due to electron correlation.

^c For $\langle q^n \rangle$, the "Total" value is defined as $\frac{1}{2}\sum_{i>j}^4 \langle q^n \rangle_{ij}$, where (i, j) denotes a pair of occupied HF molecular spin-orbitals ϕ_i and ϕ_j in momentum space for LiH.

of the Coulomb shift implies that, as discussed elsewhere,⁷ the presence of a doubly occupied orthogonal $2s$ orbital inhibits radial correlation and emphasizes the *angular* component. Therefore, by comparison, we conclude that for the $1\sigma^2(^1\Sigma)$ shell in LiH the radial constraint imposed by the 2σ orbital is minimal. This is in keeping with Li becoming, in the main, Li^+ as a consequence of molecular formation. When p_{12} is large, both Δf curves in Fig. 1(A) cross the axis at $p_{12} \approx 6$. For Be, this feature agrees with that found^{4,5} for the K shells in a series of He- and Li-like ions: namely, the crossover of each Coulomb shift was brought into common coincidence when the *scaled* coordinate $Z^{-1}p_{12} \approx 1.5$, where Z is the nuclear charge. Thus, for $1\sigma^2(^1\Sigma)$ at large p_{12} we find that, in contrast with the behavior at small p_{12} , $\Delta f(p_{12})$ suggests an "effective central" $Z \approx 4$. We also note that the *first* crossover point in $\Delta f(p_{12})$ for $1\sigma^2(^1\Sigma)$ coincides with the location of the peak in the corresponding $f_{\text{HF}}(p_{12})$.

The Coulomb shift for $2\sigma^2(^1\Sigma)$ in Fig. 1(B) possesses $\Delta f(p_{12})$ values at maximum and minimum which are approximately a tenfold increase on those for $1\sigma^2(^1\Sigma)$; however, the p_{12} range is considerably reduced. This relationship is reflected in the Υ values in Table I where the ratio $\Upsilon(2\sigma^2) : \Upsilon(1\sigma^2)$ is about 3:1. Compared with $1\sigma^2(^1\Sigma)$, the large negative value in the $2\sigma^2(^1\Sigma)$ curve indicates a significant increase in the relative importance of radial correlation; a feature also observed⁴ when comparing the Coulomb shift for H^- with that for Li^+ . Indeed, the general shape of the $2\sigma^2(^1\Sigma)$ curve is similar to that found for H^- with the first crossover occurring at $p_{12} \sim 0.7(2\sigma^2)$ and about $0.6(\text{H}^-)$, each value being the location of the corresponding $f_{\text{HF}}(p_{12})$ peak. This indicates, not surprisingly, that the outershell in LiH contains a sizeable H^- component.

A comparison between the Coulomb shifts for $2\sigma^2(^1\Sigma)$ and the $\text{LaL}\beta(^1S)$ shell in Be revealed quite different correlation characteristics. For Be, the shift has large positive values at small p_{12} indicating a highly dominant angular effect. This effect arose from the near $2s-2p$ degeneracy in Be and as such was nondynamical in origin. Proceeding to the isoelectronic example LiH reduces the symmetry and hence resolves the degeneracy, thereby diminishing the angular effect.

In contrast with the Coulomb shifts for the intrashell electron pairs, the results for $1\sigma 2\sigma(^1\Sigma \text{ and } ^3\Sigma)$ in Fig. 1(C) are as yet more difficult to interpret. Even for a series of Li-like ions, the analysis of correlation effects in momentum space for intershell electrons pairs proved to be complex.^{5,6} Nevertheless, some general comments are possible. Although the molecular inter- and intrashell curves are quite different, it is seen that both intershells have a $\Delta f(p_{12})$ range commensurate with the $1\sigma^2(^1\Sigma)$ shift. We also note that the presence of the Fermi effect in $1\sigma 2\sigma(^3\Sigma)$ yields negligible values for $\Delta f(p_{12})$ when $p_{12} < 0.25$. In addition, compared with the singlet case, the triplet curve has a larger crossover value for p_{12} followed by a *deeper* negative region.

In Table I, the relation between the CI and HF values for $\langle p_{12}^n \rangle$ for a given shell supports the above observations. Further, not only is the standard deviation $\sigma(p_{12})$ for the $1\sigma^2(^1\Sigma)$ shell larger than that for $2\sigma^2(^1\Sigma)$, highlighting the

relative diffusiveness of the corresponding $f(p_{12})$ distributions, but we also see that the correlation-induced changes in $\sigma(p_{12})$ are similarly ordered. The influence of correlation on $\sigma(p_{12})$ for the intershells produces a slight reduction in each case. For $\langle p_{12}^n \rangle$, Table I shows that correlation increases each intrashell value, with the changes in $\sigma(p_{12})$ indicating an expansion of the corresponding radial momentum distributions; this is concomitant with contractions of the intrashell charge clouds in position space. We note that the correlation-induced changes for $2\sigma^2(^1\Sigma)$ exceed those for $1\sigma^2(^1\Sigma)$, a finding which is particularly noticeable for $\langle p_{12}^{-1} \rangle$. Such observations follow from the 2σ electrons being energetically less tightly bound.

In Fig. 2, the normalized sum total Coulomb shift for LiH is seen to be dominated at small and large p_{12} by the $2\sigma^2(^1\Sigma)$ and $1\sigma^2(^1\Sigma)$ contributions, respectively. Clearly, the major influence of correlation occurs at low p_{12} and represents an expansion of the p_{12} distribution towards slightly larger p_{12} . The Υ value for LiH is also seen to follow the $2\sigma^2(^1\Sigma)$ result. This suggests that, in position space, some considerable contraction of the charge cloud has occurred in the outer regions of the molecule due to the introduction of electron correlation. This is in accord with the charge density analysis for LiH carried out earlier by Banyard and Hayns²⁵; see also Politzer and Brown.²⁶

IV. SUMMARY

Coulomb shifts are reported in brief for LiH, this being the first study of intra- and intershell electron pair correlation effects for a molecule in momentum space. Comparisons are made with a similar examination of Be.

Although the correlated wave function²³ used here for LiH is, energetically, slightly less favorable than some others,²⁷⁻²⁹ it has the convenience of being written in the CI form with a leading term of HF quality; moreover, its STO basis set is easily transformed into momentum space. However, since this CI description uses a limited number of angularly dependent basis functions, the Coulomb shifts may perhaps reflect this by exaggerating the relative importance of radial correlation.

Interpretation of the present work clearly supports the large ionic content in the description of LiH. Electron correlation is found to increase the momentum, especially so for the more loosely bound 2σ electrons. This latter result is

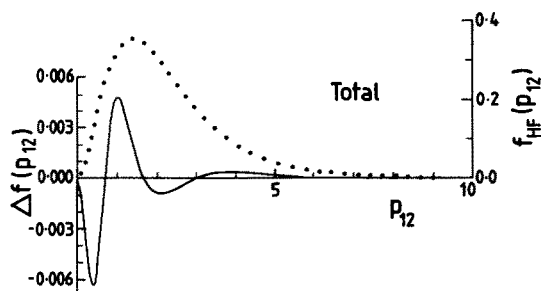


FIG. 2. The normalized sum total Coulomb shift for LiH, defined as $\Delta f(p_{12}) = \frac{1}{2} \sum_{i,j} \Delta f_{ij}(p_{12})$, is shown as — and the corresponding $f_{\text{HF}}(p_{12})$ curve is indicated by ···.

commensurate with a contraction of the outer regions of the charge density in position space.

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