Molecular Description of Two-Electron Atoms

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We show that the use of the interelectronic vector as adiabatic axis allows two-electron states of atoms to be described in terms of molecular orbitals. The associated potential curves can be obtained by scaling calculations on the $H_2{}^+$ molecular ion and show for *doubly excited* states a strong similarity to adiabatic curves obtained from an analysis in hyperspherical coordinates. We associate a definite molecular symmetry with each two-electron state.

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The three-body Coulomb problem of two nuclei and one electron, exemplified by the $H_2{}^+$ molecular ion, is the fundamentally simplest problem of quantum chemistry. The usual approach to the solution of its internal motions is first to solve the Born-Oppenheimer problem for the energy levels of the electron in the field of two stationary nuclei, then to allow the nuclei to vibrate in the potential well provided by the sum of electronic and nuclear potential energy, and finally to consider the rotation of the triangle formed by the three particles from the body-fixed frame to the laboratory frame. The natural internal coordinates for such a scheme are the Jacobi coordinates of the internuclear vector **R** and the coordinate **r** of the electron relative to the center of mass of the two nuclei. The use of such relative two-particle coordinates has the obvious advantage that the character of the internal motions can be readily visualized. The density patterns of the electronic eigenstates, the correlation diagrams of electronic levels, the vibrational wave functions for bonding and antibonding levels, and the rotation-vibration structure form the everyday language of molecular quantum mechanics.

The two-electron atom is another three-body Coulomb problem of fundamental interest. The "old-fashioned" method of attack is to solve for the motion of each electron separately in the field of the nucleus and to form approximate eigenstates as products of such solutions. Correlation between the electrons is then introduced implicitly by consideration of linear combinations of such product states or explicitly by inclusion of functions of the interelectronic separation $\mathbf{R}=\mathbf{r}_1-\mathbf{r}_2$. An alternative approach to the two-electron atom which has received wide application and development over the last few years is the use of hyperspherical coordinates.[1-5] Here the "size" of the atom is measured by a hyperradius $\mathcal{R}=(r_1^2+r_2^2)^{1/2}$ while correlation is measured by Euler angles and a hyperangle determined by the ratio r_2/r_1. The use of $\mathcal{R}$ as an adiabatic coordinate allows a description to be developed in which states are defined as vibrational levels in adiabatic energy curves as a function of $\mathcal{R}$.

The adiabatic hyperspherical method has been extremely useful in the description of doubly excited states of atoms and the particular highly correlated motion which occurs when the three-body system has zero total energy. This threshold configuration is well described by hyperspherical coordinates, but that these coordinates are by no means essential has been demonstrated before.[6] Moreover, it was recognized long ago that a "molecular" description of a two-electron atom could be given.[7,8] In this case the interelectronic separation is the adiabatic distance **R** and the vibrational potential curves correspond to different states of relative motion of the center of mass **r** of the two electrons with respect to the nucleus. Such a picture would seem to be a poor description of the ground states of helium and H^-. Nevertheless, the zeroth-order energies emerging from a *molecular* atomic model are surprisingly good.[9]

Here we show that for highly correlated two-electron systems, such as He, H^-, or even Ps^-, the zeroth-order molecular adiabatic curves provide remarkably accurate descriptions of the character and existence of doubly excited states. Since two-electron atoms have the structure of a homonuclear molecular ion with the roles of nuclei and electrons reversed, the molecular orbital (MO) energies as a function of R can be obtained simply by scaling of those of $H_2{}^+$. From this scaling property one sees that the principal differences in character between the bound and low-lying resonance states of different two-electron systems arise from the different energies of "united-atom" ($R\rightarrow 0$, two electrons together) and "separated-atom" ($R\rightarrow\infty$, one electron bound, the other at infinity) limits of the MO correlation diagram. For doubly excited states, electron correlation would appear to stiffen the line **R** joining the two electrons. This "internuclear" axis and occurrence of the Wannier ridge[4,6] could account for the method's usefulness, despite the apparent lack of an expansion parameter in the atomic case analogous to the ratio of electron mass to nuclear mass in the molecular case.

The basic picture corresponding to the adiabatic separation in electronic coordinates **R** and **r** is the following. The position of the two electrons and the nucleus defines a triangle with one apex fixed at the nucleus. The motion of the center of mass of the two electrons relative to the nucleus is described by a solution of the adiabatic MO problem. For a given MO, the change in the *magnitude* of **R** is described by a vibrational wave function. Finally, the vibrating triangle can rotate in space. It is clear that this picture is likely to be a good one when the three separate types of motion are relatively decoupled, that is, when no rapid shear deformations or changes in surface area of the triangle occur. The basic wave functions describing these three motions can be written as

$$\Psi(nlKLS) = f_{nlKL}(R)\,\phi_{nlKt}(\mathbf{r},R) \times D^{L}_{MK}(\psi,\theta,\phi)\,\chi(SM_s). \tag{1}$$

Here, LS coupling is used, $\chi(SM_s)$ is a two-electron spin wave function, and D^L_{MK} is a matrix element of the rotation operator describing the transformation from a space-fixed to a body-fixed frame by Euler angles ψ, θ, ϕ.[6] The projection K of the total orbital angular momentum along **R** is the same as the projection of the orbital angular momentum of the center of mass of the two electrons relative to the nucleus along **R**. This projection quantum number labels the MO wave functions $\phi_{nlKt}(\mathbf{r},R)$ as $\sigma, \pi, \delta \ldots$ according as $|K| = 0, 1, 2 \ldots$. The quantum number t signifies the symmetry of the MO under interchange of the two electrons. By convention from the $H_2{}^+$ problem, even symmetry is denoted by g ($t=0$) and odd symmetry by u ($t=1$). The quantum numbers n and l order the MO of a given symmetry according to energy and designate the "united-atom" principal and orbital quantum numbers of the atomic orbital to which the MO correlates as $R \rightarrow 0$. The wave function $f_{nlLK}(R)$ describes the vibrational motion of the interelectronic axis. The basic wave functions (1) are not, of course, eigenfunctions of the full Hamiltonian but are coupled together by nonadiabatic and Coriolis couplings. From a consideration of the transformation properties of the wave functions (1), one can show that eigenfunctions of the electron exchange operator P_{12} and parity operator P can be constructed from the combination

$$\phi_{nlKt}\{D^L_{MK} + (-1)^{L+T} D^L_{M-K}\}, \tag{2}$$

with $T=0$ or 1.[10] These are eigenfunctions of P_{12} with eigenvalues $(-1)^{T+t+K}$ and eigenfunctions of P with eigenvalues $(-1)^{T+K}$. That MO are further characterized by a separation constant, given as the eigenvalue of a *two-center* Runge-Lenz–type operator, distinguishes the present approach from similar ones based on single-center Runge-Lenz vectors.[11,12]

The two-electron states and their associated symmetries can then be obtained quite simply by a consideration of the ordering of the MO provided by the correlation diagram. The lowest two MO are the $1s\sigma_g$ and $2p\sigma_u$ pair correlating to the $1s$ separated-atom limit. The $1s\sigma_g$ has $K=0$, $t=0$ and from the above eigenvalues gives rise to ${}^1S^e, {}^3P^o, {}^1D^e \ldots$ series with increasing total angular momentum $L = 0, 1, 2, \ldots$. The $2p\sigma_u$ "antibonding" MO has $K=0$, $t=1$ and therefore gives rise to atomic states ${}^3S^e, {}^1P^o, {}^3D^e$ with increasing L. Already at this stage the "molecular" explanation of atomic structure emerges. For example, the lowest singlet state ${}^1S^e$ is based on the bonding $1s\sigma_g$ MO, whereas the lowest triplet state ${}^3S^e$ is based on the promoted antibonding $2p\sigma_u$ MO. This explains immediately why the triplet state in helium lies so far above the singlet ground state and why the ${}^1S^e$ state of H^- is bound but the ${}^3S^e$ state is not.

The MO occur in pairs of g,u symmetry and each pair separates to a well-defined Stark state. Higher MO separate to an atom in the $n=2$ state. For example, the $2s\sigma_g, 3p\sigma_u$ pair and the $3d\sigma_g, 4f\sigma_u$ pair have lowest states ${}^1S^e, {}^3S^e$, as do the $1s\sigma_g, 2p\sigma_u$ pair. States with $K \neq 0$ occur first in the $3d\pi_g, 2p\pi_u$ pair. From the allowed eigenvalues of parity and permutation symmetry one finds that the lowest states based on these MO must have $L=1$ but can have either spin; i.e., the $3d\pi_g$ MO gives rise to $L=1$ series of character ${}^1P^e$ and ${}^3P^o$ and the $2p\pi_u$ MO to series of character ${}^3P^e$ and ${}^1P^o$.

The adiabatic potential-energy curves supporting the vibrational and rotational motion are obtained from the MO energies[13] by addition of other correction terms. The final shape of the curves decides the character of internal motion associated with a particular symmetry. In the $H_2{}^+$ case it is usually sufficient to add the internuclear repulsion term $1/R$ to the MO energy to give Born-Oppenheimer (BO) potential curves. This is because the expectation value of the non-BO operator $-\nabla^2_R/2\mu_{12}$, i.e., diagonal coupling, is small in this case since μ_{12} is the reduced mass of the two protons (in units of the electron mass). In the case of two electrons, although the internuclear potential energy is trivially replaced by the same $1/R$ interelectronic potential energy, the diagonal coupling cannot be neglected since the electrons have a reduced mass $\mu_{12} = \frac{1}{2}$ and $1/\mu_{12}$ is no longer a small number. One effect of the omission of this correction is that the MO energies do not have the correct asymptotic limits, a deficiency which has been recognized for a long time.[7,14,15] The scaling of the MO wave functions and energies and inclusion of the diagonal coupling can serve, however, to correct this deficiency. An optimum scale parameter at each R can be determined variationally by our minimizing at each R the adiabatic energy with diagonal coupling. We have found[9] that this scale parameter is, however, a slowly varying function except for small R where the $1/R$ potential, which does not scale, dominates. For the present we thus find it adequate to determine the scale once and for all as $R \rightarrow \infty$. Then, the resulting adiabatic energy curves have exactly the correct asymptotic limits.[7]

A feature, not usually of importance in the H_2^+ problem, is that the diagonal coupling introduces an explicit dependence on the quantum numbers L and K into the adiabatic molecular curves. Hence, curves of quite different character are obtained from states of different L based on the same MO. This is readily seen from the approximate large-R form of the expectation value of $-\nabla_R^2/2\mu_{12}$, which, denoted by $C(R)$, has the property[16]

$$C(R) \simeq 1/4n^2 + \{L(L+1) - 2K^2\}/R^2 \qquad (3)$$

for large R. In fact, we have used this approximate form in constructing the adiabatic potential curves we present here, since only in one case $2p\pi_u$ have we found in the literature accurate values of $C(R)$ for all R.[17] Hence, except for this case, the quantitative accuracy of our results is limited at the present time. However, it is not likely that a subsequent more accurate evaluation will seriously alter any qualitative predictions since again all curves at small R, where the approximation (3) fails, are dominated by the $1/R$ interelectronic repulsion.

Our adiabatic potential curves for the states of H^- separating to $n=2$, obtained with $C(R)$ from Eq. (3), are shown in Fig. 1. From the symmetry properties of the wave functions (2), states of ${}^1P^o$ symmetry are obtained from the $3p\sigma_u$, $4f\sigma_u$, and $2p\pi_u$ MO and shown in Fig. 1(a). They display a remarkable similarity to the hyperspherical curves in Fig. 2 of Lin[2] and allow molecular symmetry assignments to be given to those curves. For example, the $3p\sigma_u$ MO is antibonding and gives a fully repulsive potential curve (labeled "*pd*" by Lin). The $4f\sigma_u$ is similarly a promoted MO but has at large R sufficient $2p$ character to be first depressed in energy and give rise to a shallow minimum. This is the "−" state of Lin's classification[2,4] giving rise to a series of Feshbach resonances in e^--H scattering. The $2p\pi_u$ MO is a bonding orbital and therefore has a deeper minimum, but the different nature of the long-range Stark splitting in the π case gives rise to a slight maximum. Hence, this "+" state which supports a shape resonance is of $2p\pi_u$ MO character. An important point to note is that the $2p\pi_u$ and $4f\sigma_u$ curves have a real crossing because of their different MO symmetries.[18] By contrast, the corresponding adiabatic hyperspherical curves have an avoided crossing,[2-4] and crossing is only forced by inclusion of off-diagonal coupling.

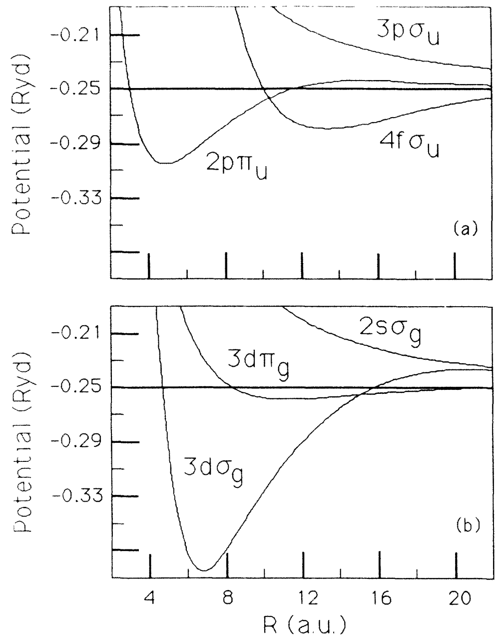

FIG. 1. The adiabatic potential energy curves of the (a) ${}^1P^o$ and (b) ${}^3P^o$ states of H^- correlating to the $n=2$ level of H.

The *gerade* partners of $3p\sigma_u$, $4f\sigma_u$, and $2p\pi_u$, namely $2s\sigma_g$, $3d\sigma_g$, and $3d\pi_g$, support states of ${}^3P^o$ symmetry whose potential curves are shown in Fig. 1(b). Again, inspection of Fig. 2 of Lin[2] shows that these curves correspond respectively to this "*pd*," "+," and "−" classification of the ${}^3P^o$ states. The $2s\sigma_g$ MO is the highest lying of the six $n=2$ MO at large distances and, therefore, is wholly repulsive. By contrast, the $3d\sigma_g$ MO increases its binding energy strongly at intermediate R (it tries to stay $2p$-like) with the result that the corresponding potential curve has a deep minimum. This is the "+" ${}^3P^o$ curve of Fig. 2 of Lin.[2] The "−" curve has $3d\pi_g$ MO character and in our case has a shallow minimum in contrast to Lin's result.[2] At this level of sophistication in our calculation it is not possible to say that this minimum is real. A more accurate form of the diagonal coupling than provided by (3) may make this curve more repulsive. In addition, the $3d\pi_g$ and $3d\sigma_g$ MO will mix by off-diagonal rotational coupling and the real crossing shown in Fig. 1(b) will become avoided, pushing down the $3d\sigma_g$ MO. By contrast, the adiabatic hyperspherical "+" ${}^3P^o$ curve exhibits the proper long-range attractive dipolar form. Finally, we find that the ${}^1P^e$ and ${}^3P^e$ pair of curves of Fig. 4 of Lin[2] arise simply from

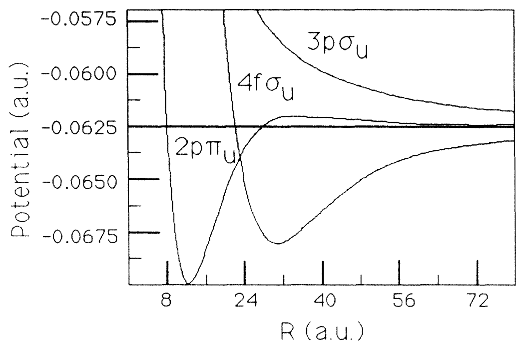

FIG. 2. The adiabatic potential energy curves of the $^1P^\circ$ states of Ps^- correlating to the $n=2$ level of Ps.

the lowest *even-odd* pair of MO of π symmetry, namely, the $3d\pi_g$ and $2p\pi_u$.

In the one case of the $2p\pi_u$ MO, the diagonal coupling matrix element $C(R)$ is available in the literature,[17] and a more accurate scaling can be made. The principal effect of this correction on the potential is to lift the minimum up and push it out to larger R, leaving the qualitative shape in Fig. 1(a) unchanged.[18] We find the potential barrier to peak around $R=16$ a.u., 6.8×10^{-3} Ry above the $H(n=2)$ threshold, and estimate a $^1P^\circ$ shape resonance at 40 meV above threshold in fair agreement with Lin's hyperspherical determination of a $^1P^\circ$ shape resonance at 28 meV.[2]

Finally, in Fig. 2 we have rescaled our H^- curves to describe doubly excited states in Ps^-. The resulting potentials are qualitatively similar to those obtained in H^- and very similar to hyperspherical Ps^- curves calculated recently by Botero and Greene.[19] In particular, our more accurate[17] $2p\pi_u$ $^1P^\circ$ potential has near $R=40$ a.u. a maximum barrier height of 6.8×10^{-4} a.u. above the $Ps(n=2)$ threshold, and we estimate a $^1P^\circ$ shape resonance at 3.5×10^{-4} a.u. above threshold somewhat lower than Botero and Greene's determination of a $^1P^\circ$ shape resonance at 4×10^{-4} a.u.

To summarize, we have obtained adiabatic potential curves for two-electron systems by scaling matrix elements calculated for the H_2^+ molecular ion. In the case of double excitation, we have demonstrated a close similarity of our curves with ones calculated as a function of hyperspherical radius. The molecular description, however, allows us to associate a definite MO symmetry to each curve and to explain electron correlations and nonadiabatic effects in terms of familiar molecular concepts of long-range Stark splittings, bonding or antibonding character, and radial and rotational couplings.

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[1] J. Macek, J. Phys. B **1**, 831 (1968).

[2] C. D. Lin, Phys. Rev. A **16**, 30 (1976).

[3] H. Klar and M. Klar, J. Phys. B **13**, 1057 (1980).

[4] U. Fano, Rep. Prog. Phys. **46**, 97 (1983).

[5] C. H. Greene, J. Phys. B **13**, L39 (1980).

[6] J. M. Feagin, J. Phys. B **17**, 2433 (1984).

[7] G. Hunter, B. F. Gray, and H. O. Pritchard, J. Chem. Phys. **45**, 3806 (1966).

[8] G. Hunter and H. O. Pritchard, J. Chem. Phys. **46**, 2146, 2153 (1967).

[9] J. M. Feagin, J. S. Briggs, and T. P. Weissert, in *Abstracts of the Contributed Papers of the Fourteenth International Conference on the Physics of Electronic and Atomic Collisions,* edited by M. J. Coggiola, D. L. Huestis, and R. P. Saxon (North-Holland, Amsterdam, 1985), p. 147.

[10] A. K. Bhatia and A. Temkin, Phys. Rev. **137**, 1335 (1965). This reference gives an analogous atomic decomposition of the H_2^+ MO, although using coordinates r_1 and r_2 and another set of Euler angles.

[11] D. R. Herrick and M. E. Kellman, Phys. Rev. A **21**, 418 (1980).

[12] M. Crance and L. Armstrong, Phys. Rev. A **26**, 694 (1982).

[13] D. R. Bates and R. H. G. Reid, Adv. At. Mol. Phys. **4**, 13 (1968).

[14] A. Fröman and J. L. Kinsey, Phys. Rev. **123**, 2077 (1961).

[15] A. Fröman, J. Chem. Phys. **36**, 1460 (1962).

[16] R. T. Pack and J. O. Hirschfelder, J. Chem. Phys. **49**, 4009 (1968).

[17] A. Dalgarno and R. McCarroll, Proc. Roy. Soc. London, Ser. A **237**, 383 (1956), and **239**, 274, 413 (1957).

[18] Our curves as a function of R are more compact than their hyperspherical counterparts as a function of $\mathcal{R}=(R^2/2+2r^2)^{1/2}$; however, accurate diagonal coupling tends to push features in our curves out to large R. For example, we find that our best $2p\pi_u$ $^1P^\circ$ curve, obtained with use of Ref. 17, actually crosses the $4f\sigma_u$ $^1P^\circ$ curve beyond $R=11.5$ a.u.

[19] J. Botero and C. H. Greene, Phys. Rev. Lett. **56**, 1366 (1986).