

Calculation of radial couplings in the model-potential and pseudopotential approaches: The NaH quasimolecule

O. M6, A. Riera, and M. Y6ñez

*Departamento de Qu6mica F6sica y Qu6mica Cu6ntica, Facultad de Ciencias C-XIV,
Universidad Aut6noma de Madrid, Cantoblanco, Madrid 34, Spain*

(Received 9 July 1984; revised manuscript received 9 October 1984)

We present an extension of the analytical method of Mac6as and Riera to calculate radial couplings, to include model potentials or (local and nonlocal) pseudopotentials, in the Hamiltonian. As an illustration, energies, couplings, and momentum matrix elements are presented and discussed for the effective two-electron NaH quasimolecule, as a stringent test case.

Model potential and pseudopotential methods, which have been successfully applied to the study of atoms and molecules,¹⁻³ are based on setting up an effective Schr6dinger equation that only treats explicitly the valence electron of a given system. This results not only in a considerable reduction of the amount of computation work, but also in great conceptual simplicity in the description of the electronic structure of that system. A very promising area of application of the valence-electron methods is the calculation of energy correlation diagrams for their use in the treatment of atomic (molecular) collisions,⁴ since these methods are much less elaborate than all-electron configuration interaction (CI) calculations, and do not present the difficulties of less accurate methods, such as the virtual excitation approach.⁵

The purpose of this Brief Report is to discuss how the techniques employed in the molecular treatment of atomic collisions can be adapted to include model potentials or pseudopotentials in the Hamiltonian. In particular, the calculation of radial couplings can be performed analytically, by a straightforward extension of the method proposed by Mac6as and Riera,⁶ provided that both the wave functions and the effective potentials are expanded in terms of Gaussian-type orbitals (GTO's). We shall prove the usefulness of this statement for the rather stringent case⁷ of the effective two-electron NaH quasimolecule, and for three different approaches: a model potential, a local, and a nonlocal (Phillips-Kleinman-type⁸) pseudopotential.

In recent years many measurements of charge exchange cross sections between hydrogen atoms and alkali-metal vapors have been carried out, especially in view of their relevance in controlled thermonuclear fusion research. In particular, capture and stripping of Na targets by incident H atoms has been reported.⁹ However, although some characteristics of the energy curves of the NaH quasimolecule are known,¹⁰ the corresponding radial couplings which are needed to tackle the charge exchange process are not available in the literature. Finally, it is also interesting to know whether, for that system, "diabatic" states can be constructed that fulfill the basic assumptions of the widely used Landau-Zener linear model. These assumptions are (i) that the "diabatic" states are orthogonal in the neighborhood of the crossing point of their energies (ii) that their radial coupling is negligible and (iii) that the transition region is so localized in the crossing region that the energy difference can be taken to be linear and the electrostatic interaction constant. As a consequence of these assumptions the corresponding adia-

batic states present, in the crossing region, a Lorentzian radial coupling whose area is $\approx \pi/2$. That these postulates are not always fulfilled for ionic-covalent transitions was first pointed out in Ref. 11, for the H₂ quasimolecule. For example, because of the failure of supposition (iii) Nikitin's¹² exponential linear model should replace^{11,13} the usual linear approach. When the radial coupling between the adiabatic states is available, a danger signal of breakdown of (iii) is given by the fact that the area under the coupling is $\ll \pi/2$. It is useful to know whether the H₂ quasimolecule is an exception, or whether the Landau-Zener approach is *a priori* questionable for other systems.

To calculate the NaH molecular energies, we have solved an effective Schr6dinger equation of the form (atomic units are used throughout)

$$\left[-\frac{1}{2} \sum_{i=1}^2 \nabla_i^2 + \sum_{i=1}^2 \left(V_{\text{eff}}(r_{Ai}) - \frac{1}{r_{Bi}} \right) + \frac{1}{r_{12}} + V_{\text{NaH}^2+}(R) \right] \psi_n = E_n \psi_n, \quad (1)$$

where r_{Ai} is the distance of electron i from the Na nucleus within the manifold spanned by a basis set of symmetry-adapted configurations built from GTO's centered on each nucleus; the atomic basis set is presented in Table I.

Three choices for the effective potential V_{eff} were selected.

(1) A model potential of the form

$$V_M(r) = -\frac{10}{r} (1 + \alpha r) e^{-2\alpha r} - \frac{1}{r}, \quad (2)$$

where $\alpha = 1.83$ is a parameter that was chosen so as to (least-squares) fit, for $R \rightarrow \infty$, the energies of the first two states of separate atom limit of the quasimolecule. As explained in Ref. 7, the effective Hamiltonian of Eq. (1) supports, for $V_{\text{eff}} = V_M$, an infinite number of low-lying "virtual" or "core" states,² represented by $\mathcal{A}(\phi_n \psi_m)$, where \mathcal{A} is the antisymmetrizer, ϕ_n a virtual state of the model potential (2), and ψ_m a hydrogen eigenfunction. This striking feature is common to all many-electron model potentials; obviously, when solving (1) within the manifold spanned by the configuration basis set, one only reproduces a finite (basis-dependent) number of core states; a detailed discussion of this property of model potentials would lengthen this Brief Report unnecessarily and will be presented elsewhere.

(2) To the model potential of (2) a nonlocal Phillips-

TABLE I. Exponents of the atomic basis set of GTO's used in the calculation.

Model potential				Local pseudopotential			
Na	H		Na	H			
α_{1s}	α_{2p_z}	α_{1s}	α_{1s}	α_{2p_z}	α_{1s}	α_{2p_z}	
300.0	8.5	10.6	9.1	8.5	10.6	3.2	
50.0	1.55	2.8	1.65	1.55	2.8	0.7	
9.1	0.28	0.6	0.30	0.28	0.6	0.25	
1.65	0.05	0.16	0.05	0.05	0.16		
0.30	0.01	0.04	0.01	0.01	0.04		
0.05							
0.01							

Kleinman⁸ pseudopotential was added

$$V_{PS} = - \sum_{n=1}^{N_c} |\phi_n\rangle \epsilon_n \langle \phi_n|, \quad (3)$$

where the summation runs over all atomic core states of the model potential (2), of energies ϵ_n , and wave functions ϕ_n . The addition of V_{PS} of (3) to V_M of Eq. (2) has the effect of shifting the virtual molecular states represented by A ($\phi_n \psi_m$) to higher energies.

(3) A local pseudopotential

$$V_{LPS} = - \frac{10}{r} (1 - \beta r) e^{-2\alpha r} - \frac{1}{r} \quad (4)$$

was chosen with a form similar to (2). The parameters $\alpha = 1.887$ and $\beta = 9.613$ were chosen so as to fit, for $R \rightarrow \infty$, the energies of the first four states of the separated atom limit of the quasimolecule. Then, the fact that α takes up practically the same value for V_M as for V_{LPS} indicates the physical relevance of both potentials [hence, of the corresponding wave functions in (1)], since their attractive parts for $R > 2.5$ a.u. are identical, and they only differ in the core region.

Our main point is that, for the three effective potentials (1), (2), and (3), the matrix elements $\langle \psi_n | \partial / \partial R | \psi_m \rangle$ can be calculated *analytically*, provided that a set of GTO's is employed to construct the basis configurations. The pertinent equations that yield the couplings are given in Refs. 5 and 6 and will not be repeated here. The only new terms that are required here are the derivatives of V_{NaH2+} and of the matrix elements of V_{eff} , with respect to the internuclear distance. For the former, the (analytic) asymptotic form of the potential is a good approximation to V_{NaH2+} for the whole range of internuclear distances of interest, and this asymptotic form can be differentiated. By expansion of the exponential $e^{-2\alpha r}$ in terms of GTO's (e.g., a six-term expansion is extremely accurate¹⁴), the matrix elements of V_M [Eq. (2)] and V_{LPS} [Eq. (4)] are expressed in terms of overlap and nuclear attraction matrix elements involving three GTO's, which can be analytically evaluated¹⁵ and differentiated. Likewise, the derivative of the matrix elements of V_{PS} [Eq. (3)] can be expressed in terms of overlap integrals and matrix elements of the d/dR operator between GTO's; the calculation of these matrix elements is explained in Ref. 6. When the origin of electronic coordinates is shifted by an amount $R\delta$, the radial couplings change⁶ by $\delta \langle \psi_n | iP_z | \psi_m \rangle$, where P_z is the component of the electronic linear momentum along the internuclear axis. The calculation of these matrix elements can be carried out as in the standard case.⁵

To calculate the radial couplings between the (approximate) solutions of Eq. (1), the programs that are normally employed at our laboratory to evaluate couplings were appropriately modified, following the lines of the previous paragraph. Our results for the molecular energies, radial couplings, and iP_z matrix elements are presented in Figs. 1, 2, and 3, respectively, and for the three approaches (1), (2), and (3).

For short internuclear distances ($R < 4$ a.u.), it will be noticed in Fig. 1 that the energy levels calculated with the model potential approach collapse to lower energies. We

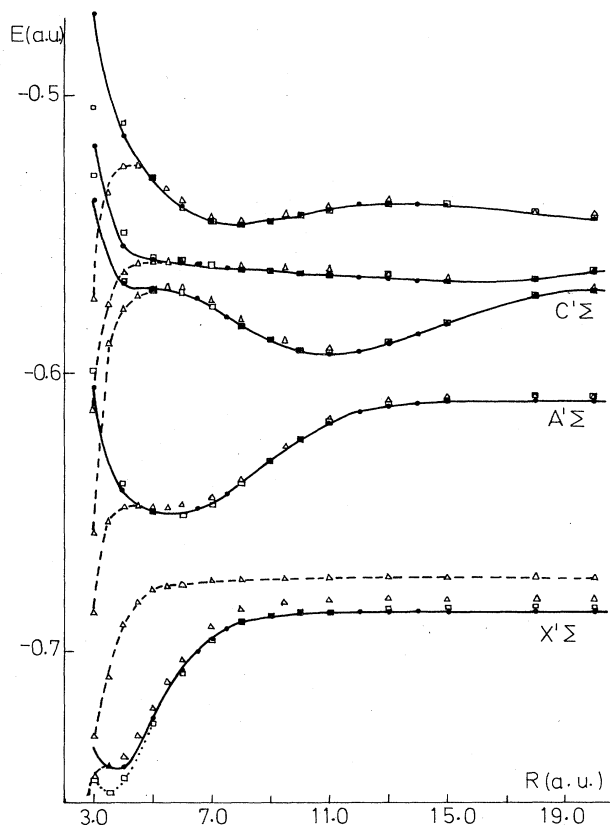


FIG. 1. Molecular energies; \bullet , local pseudopotential [Eqs. (1) and (4)]; Δ , model potential [Eqs. (1) and (2)]; \square , addition of a nonlocal pseudopotential [Eq. (3)], to the model potential; $- - -$, poorly reproduced virtual states (see text). *Ab initio* results of Ref. 10 are not shown since they fall exactly on the solid line.

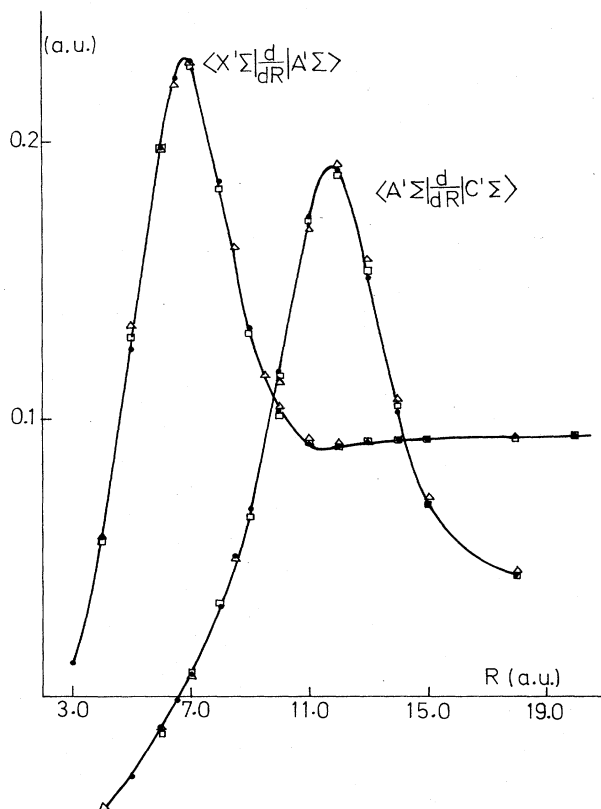


FIG. 2. Radial couplings. Origin at the center of core charge (symbols as in Fig. 1).

have carefully checked that this collapse is *not* due to quasi-linear dependences in the two-center basis set of Table I, since in our calculations all configurations that were even weakly linearly dependent (as shown by the eigenvalues of the overlap matrix) were eliminated from the basis set. In fact, the collapse is a general phenomenon for two (or more) electron model potentials, and its origin, explained in Ref. 7, will be discussed in detail elsewhere, as it is not relevant to the aim of this Brief Report. Essentially it is due to the property of two-center atomic basis sets of being able to describe more core states [and there is an infinite number of them for the exact solution of (1)] for short than for large R . A further proof of this interpretation is afforded by the fact that addition of the nonlocal pseudopotential V_{PS} suppresses the collapse, since then all virtual states lie above the $X^1\Sigma$ state.

Most interestingly, the region of internuclear distances ($R > 4$ a.u.) that is important in the treatment of the charge exchange process $\text{Na} + \text{H} \rightarrow \text{Na}^+ + \text{H}^-$ is very well treated by the three approaches (1), (2), and (3), which yield very close results. The ground $X^1\Sigma$ state corresponds to the first eigenvalue of the effective Hamiltonian of Eq. (1) for $V_{\text{eff}} = V_M + V_{PS}$ and for $V_{\text{eff}} = V_{LPS}$. For the basis set of Table I, it corresponds to the 15th eigenvalue for $V_{\text{eff}} = V_M$, the 14 first eigenvalues being virtual ones; also the 16th eigenvalue for $V_{\text{eff}} = V_M$ corresponds to a virtual state that is poorly reproduced by our basis set, so that the first excited state $A^1\Sigma$ corresponds to the 17th eigenvalue; this situation is not uncommon in the use of more than one

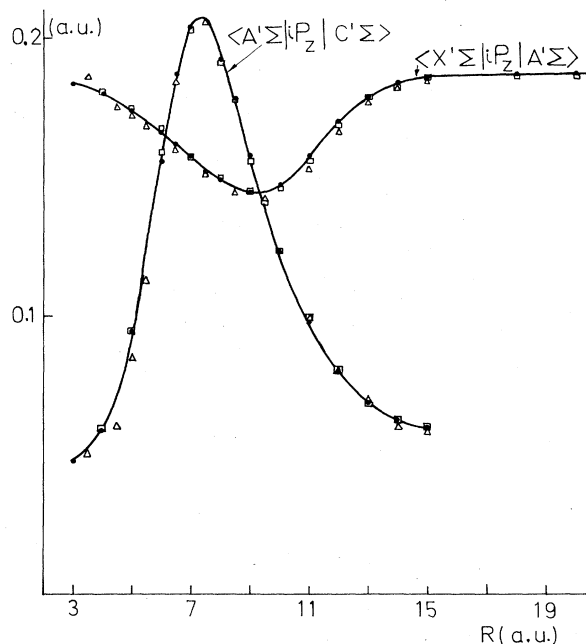


FIG. 3. Sensitivity of radial couplings to the choice of origin (symbols as in Fig. 1).

electron effective Hamiltonian in a configuration interaction framework. From all this, and given the extreme sensitivity of radial couplings to even quite small differences in the wave functions, the agreement between the d/dR matrix elements calculated by the three procedures is much more remarkable than that between the energies, and stresses the correct physical description provided by the wave functions obtained, and the stability of the radial coupling calculation.

The main feature of the radial couplings of Fig. 2 are the maxima at $R \approx 7$ a.u. and $R \approx 12$ a.u., for the $X^1\Sigma - A^1\Sigma$ and $A^1\Sigma - C^1\Sigma$ couplings, respectively, in the regions where the corresponding energy curves avoid crossing. At these pseudocrossings each of the two molecular wave functions changes character from covalent to ionic or vice versa, and nonadiabatic transitions in these regions of internuclear distances provide the basic mechanisms for the charge transfer process in $\text{Na} + \text{H}$ collisions. The fact that the area under the left half of each peak is, for any choice of origin, much smaller than $\pi/4$, indicates that assumption (iii) of the Landau-Zener model is not fulfilled. Moreover, inspection of the configuration matrix elements shows that covalent and ionic structures have a large overlap in the avoided crossing region, so that, following the argument given in Ref. 11, postulates (i) and (ii) also break down. Hence, $\text{Na} + \text{H}$ collisions are another instance where there is no theoretical justification for using the Landau-Zener method, nor for parametrizing results using this approach. Using the energies and couplings reported here, we have performed calculations of the charge exchange cross section in $\text{Na} + \text{H}$ collisions, for a $\text{H}(1s)$ impact energy range 1–10 keV, and obtained results that are of the same order as the experimental data of Ref. 9. However, they are so origin dependent that a meaningful treatment of the process clearly requires the introduction of translation factors,¹⁶ a need that is also apparent from the presence of residual couplings at infinite internuclear separation. Such a more complete col-

lision treatment with translation factors is left for a separate article. The minimum of $\langle X^1\Sigma | iP_z | A^1\Sigma \rangle$ as a function of R (see Fig. 3) is due to the fact that at $R \approx 12$ a.u., the character of the $A^1\Sigma$ state changes from ionic ($\text{Na}^+ + \text{H}^-$) to covalent [$\text{Na}(3p) + \text{H}(1s)$]; since this covalent structure is dipole coupled to the ground-state [$\text{Na}(3s) + \text{H}(1s)$] one, the iP_z matrix element tends to a constant value⁵ for $R \rightarrow \infty$. Likewise, $\langle A^1\Sigma | iP_z | C^1\Sigma \rangle$ also presents a

minimum for large R in the region where the $C^1\Sigma$ state changes character from ionic to covalent [$\text{Na}(4s) + \text{H}(1s)$], and tends to a constant value for larger internuclear distances.

We thank L. F. Errea for helping us to check the new programs that calculate radial couplings for the model potential and pseudopotential approaches.

¹The bibliography on these methods is too extensive to be given here. Many important papers are cited in Refs. 2 and 3.

²J. D. Weeks, A. Hazi, and S. A. Rice, *Adv. Chem. Phys.* **16**, 283 (1969); G. Peach, *Comments At. Mol. Phys.* **11**, 101 (1982).

³V. Bonifacic and S. Huzinaga, *J. Chem. Phys.* **60**, 2779 (1974); Y. Sakai and S. Huzinaga, *ibid.* **76**, 2537 (1982).

⁴B. C. Garrett, M. Redman, D. G. Truhlar, and C. F. Melius, *J. Chem. Phys.* **74**, 412 (1981); M. Kimura, R. E. Olson, and J. Pascale, *Phys. Rev. A* **26**, 3113 (1982); W. Fritsch and C. D. Lin, *J. Phys. B* **16**, 1595 (1983).

⁵A. Macías and A. Riera, *Phys. Rep.* **90**, 299 (1982).

⁶A. Macías and A. Riera, *J. Phys. B* **10**, 861 (1977); **11**, 1077 (1978).

⁷O. Mó and A. Riera, in *Abstracts of Proceedings of the XIIIth International Conference on the Physics of Electronic and Atomic Collisions, Berlin, 1983*, edited by J. Eichler, W. Fritsch, I. V. Hertel, N. Stoltefoht, and U. Wille (ICPEAC, Berlin, 1983), p. 315.

⁸J. C. Phillips and L. Kleinman, *Phys. Rev.* **16**, 287 (1959).

⁹A. M. Howald, R. E. Miers, J. S. Allen, L. W. Anderson, and Chun C. Lin, *Phys. Rev. A* **29**, 1083 (1984).

¹⁰R. E. Olson and B. Liu, *J. Chem. Phys.* **73**, 2817 (1980); S. C. Yang, D. D. Nelson, Jr., and W. C. Stwalley, *ibid.* **78**, 4541 (1983); O. Nedelec and M. Giroud, *ibid.* **79**, 2121 (1983).

¹¹F. Borondo, A. Macías, and A. Riera, *J. Chem. Phys.* **74**, 6126 (1981).

¹²E. E. Nikitin, *Adv. Quantum Chem.* **5**, 185 (1970).

¹³F. Borondo, A. Macías, and A. Riera, *Chem. Phys.* **81**, 303 (1983).

¹⁴R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.* **51**, 2657 (1969); **54**, 724 (1971).

¹⁵S. F. Boys, *Proc. R. Soc. London, Ser. A* **200**, 542 (1950); I. Shavitt, *Methods Comput. Phys.* **2**, 1 (1963).

¹⁶J. B. Delos, *Comments At. Mol. Phys.* **10**, 211 (1981); A. Riera, *ibid.* **12**, 95 (1982).