International Journal of Theoretical Physics, Vol. 24, No. 2, 1985

Adiabatic Approximation for W^* Quantum Systems with Particles of Mass m, M as $(m/M)^{1/2} \to 0$

Hans H. Grelland[1]

Received March 2, 1984

The $(m/M)^{1/2} \to 0$ limit and the adiabatic approximation for a nonrelativistic system consisting of light and heavy particles of masses m, M are studied. The method used involves a standard representation of quantum mechanics, in which the limit above exists. The standard representation is described in some detail, and the Primas-Raggio theorem is derived, which implies that the limit $(m/M)^{1/2} \to 0$, the heavy-particle system is a static, semiclassical system, i.e., with a commutative algebra of observables. The adiabatic approximation is derived as the leading correction.

1. INTRODUCTION

As a motivation for the present study, we first consider some heuristic arguments concerning systems consisting of light particles with mass m and heavy one with mass $M = m/\varepsilon^2$, where ε is small and dimensionless. The Heisenberg uncertainty relations for the heavy particles

$$\Delta x \Delta p \geq \frac{\hbar}{2} \tag{1}$$

can be put on a form which is easier to interpret kinematically,

$$\Delta x \Delta v \geq \frac{\hbar \varepsilon^2}{2m} \tag{2}$$

by the relation $p = Mv$. Here we see that a localized particle has an indefinite velocity, but less indefinite the heavier it is. The characteristic properties of very heavy particles may be approximated by the limit $\varepsilon \to 0$ (i.e., $M \to \infty$), subject to the constraint that the energy is kept finite. This assumption entails

$$\left\langle \frac{p^2}{2M} \right\rangle \text{finite} \Rightarrow \langle \varepsilon p \rangle \qquad \text{finite as } \varepsilon \to 0 \tag{3}$$

[1]Department of Chemistry, University of Oslo, Blindern-Oslo 3, Norway.

0020-7748/85/0200-0179$04.50/0

Thus,

$$\langle p\rangle \to \infty \quad \text{and} \quad \langle v\rangle \to 0 \qquad \text{for } \varepsilon \to 0 \tag{4}$$

consistent with (2). However, because of (4), the uncertainty relations involving p or v are of less interest than an intermediate version involving the finite quantity εp:

$$\Delta x \Delta(\varepsilon p) \geqslant \frac{\hbar}{2m} \varepsilon \to 0 \qquad \text{for } \varepsilon \to 0 \tag{5}$$

Apparently, one can infer that in the limit $\varepsilon \to 0$, one obtains a theory with dynamical variables x and $\eta \equiv \varepsilon p$, which is classical, i.e., with commuting quantities. The present paper is a detailed elaboration of this fact, together with a derivation of the adiabatic approximation for such a system.

The mathematical formalism for the study of the limit $\varepsilon \to 0$ is suggested by Primas (1980b, 1981, 1984) and Raggio, but has unfortunately not been published in detailed form. Their results, as presented in (1980b), are therefore included in Section 3 of the present paper.

The main advantage of the Primas–Raggio method is that it includes an explicit description of the limiting case $\varepsilon = 0$, in which we obtain a theory which differs in certain fundamental aspects from the theory at finite ε. In fact, as the argument above suggested, we obtain a purely classical (commutative) theory in the variables x, η for the heavy particles.

The study of this limit is made possible by a mathematical formalism which is more general than the usual irreducible Hilbert space representations of quantum mechanics, namely, the formulation in terms of W^*-dynamical systems. For the necessary background, we refer to the reviews by Primas (1980a, 1981) which include extensive reference lists. For a mathematically rigorous and detailed exposure of von Neumann algebras and standard forms, we recommended the book by Bratteli and Robinson (1979).

After a sketch of the historical background given in Section 2, we review in Section 3 the theory presented in Primas (1980b). Here the "ε representation" of the system we are considering is described. In this representation, the operator algebra is a standard form (see Bratteli and Robinson, 1979, Chapter 2.5). The limit system at $\varepsilon = 0$ is described, and it is seen to have a classical part, described by a commutative W^* algebra, and thus having a phase space representation. This part describes the heavy particles. Thus, in the molecular case, the theory sustains the notion of a classical molecular "structure," on which almost all chemical theory is based.

The theory is cast into a more complete form in Section 4. Here, the ε representation is related to the canonical standard representation of $\mathscr{L}(\mathscr{H})$.

The mapping from the usual representation of quantum mechanics to the ε representation is explicitly constructed. The limit $\varepsilon \to 0$ has some similarity to the limit $\hbar \to 0$, which is considered elsewhere (Grelland, 1984a, 1984b).

In Section 5, we proceed to the study of the leading terms in the expansion in powers of ε of the dynamics of the heavy-particle system. We obtain the adiabatic approximation. Our derivation differs, however, fundamentally from the suggestions of Primas (1980b, 1981). We have thus given a theoretical justification for the studies of nuclear potential hypersurfaces in terms of electronic energies far from the equilibrium geometry of molecules.

2. HISTORICAL OUTLINE

In the adiabatic approximation of molecular theory, the dynamics of the system is described in two steps:

(I) Relative to the electrons, the nuclei are assumed to appear as static, classical particles generating an external field, in which the electronic part can reach its stationary states for each nuclear configuration.

(II) When the nuclei move within certain well-behaving subsets U of the nuclear configuration space, the electronic eigenvalues change smoothly, generating a set of energy hypersurfaces, one for each electronic eigenvalue. In the subsets U, the electronic eigenvalues are assumed to be isolated and nondegenerate to create well-defined surfaces. The nuclei, then, move as quantum particles with one of the electronic energy surfaces together with the internuclear repulsion as a potential.

A modified version is to study the nuclear motion in a different time-scale s

$$s \equiv \varepsilon t, \qquad \varepsilon = (m/M)^{1/2} \tag{6}$$

where m, M are the electronic and (a typical) nuclear mass, respectively. This may be called the semiclassical adiabatic approximation (see below). Step (I) alone, choosing the nuclear configuration to be a minimum of the energy surface in (II) (the equilibrium condition), i.e., with a state vector for the electrons and a classical (localized) position for the nuclei, is the Born–Oppenheimer (1927) approximation.

The adiabatic approximation was described by London (1928), probably for the first time in a proper quantum mechanical context. The attempt by Born and Oppenheimer (1927) to underpin the idea was restricted by the equilibrium condition, and was only concerned with the energy spectrum and its separation into electronic, vibrational, and rotational subspectra. The theory was applied to diatomic molecules only. Later, Born (1954) replaced this derivation by a simpler and more general one (see Baym,

1969) designed to justify the adiabatic approximation. Both attempts have been criticized by Woolley (1976) and Woolley and Sutcliffe (1977). A rigorous derivation of the Born–Oppenheimer approximation for the energy spectrum of diatomic molecules, has been obtained by Combes (1977) and Combes and Seiler (1978), using modern spectral theory of operators in Hilbert spaces. Thus, the original Born–Oppenheimer problem has been solved (i.e., for diatomic molecules).

An attempt at a rigorous derivation of the adiabatic approximation as an explicitly time-dependent problem, is due to Hagedorn (1980). He uses a method designed for the study of the time-dependent $\hbar \to 0$ limit, which forces him to study the nuclear motion on the time scale s [equation (6)]. In this time scale the nuclei move adiabatically (i.e., with the electron energy a surface as potential), but they move as semiclassical particles with a renormalized mass of unit order of magnitude. Thus one is left with two problems:

(a) How can a *classical* particle produce the nuclear vibrational–rotational spectrum?
(b) The appearance of the actual nuclear mass in the equations of motion in the traditional adiabatic approximation is essential to obtain the correct spectra. If (a) could be solved, how could we obtain the same spectrum with a renormalized mass?

On the other hand, the Hagedorn solution apparently solves another problem, which we believe was originally pointed out by Woolley (1976); In the Born–Oppenheimer approximation, the nuclei are treated as classical particles. However, classical particles are incompatible with quantum mechanics, at least with stationary states. Hence, we must impose a new concept, not derivable from quantum mechanics (as it seems), to obtain the Born–Oppenheimer approximation. An extensive survey of the discussion raised by Woolley is given by Claverie and Diner (1980). As in the $\hbar \to 0$ problem, Hagedorn solves the $\varepsilon \to 0$ problem by studying finite differences within the conventional irreducible formalism of quantum mechanics, instead of taking the limit $\varepsilon = 0$, which does not exist within that formalism.

A deeper understanding of the problem was made available by some work by Primas and Raggio (Primas, 1980b, 1981) who point out that the semiclassical limit $\varepsilon \to 0$ can be derived from quantum mechanics by using a type of representation called a standard representation, i.e., a von Neumann algebra of standard form. This method is the starting point of the present paper. Moreover, Primas (1981) suggests that problem (a) can be solved in the semiclassical adiabatic approximation by stochastic methods. However, problem (b) seems to exclude the possibility of leaving

the original time scale t. The present paper therefore presents a derivation of the adiabatic approximation from the t dynamics of the molecule.

3. THE ε REPRESENTATION AND THE $(m/M)^{1/2} \to 0$ LIMIT

We now describe the representation of quantum mechanics in which we will work. For finite values of ε, this representation is equivalent to the usual irreducible Hilbert space representation, but it is based on the more abstract notion of a W^*-algebraic system. What we want to describe is a nonrelativistic system consisting of K heavy particles of mass $M_j = \lambda_j m/\varepsilon^2$ $(j = 1, \ldots, K)$ and L light particles of mass m. $\varepsilon = (m/M)^{1/2}$, where $M = M_j/\lambda_j$, is thus a dimensionless parameter of the theory. The parameters λ_j are assumed to be of unit order of magnitude.

The bounded physical quantities (bounded observables) of the system are represented by the self-adjoint elements of a W^*-algebra A, which is *-isomorphic to the set $\mathscr{L}(\mathscr{H})$ of bounded operators on $\mathscr{H}$. (A *-isomorphism is sufficient to obtain "physical equivalence" (see, e.g., Primas, 1980a, Chapters 4.4 and 5.4)). In our case, $\mathscr{H} \subseteq L^2(\mathbb{R}^{3(K+L)})$, where $\mathscr{H}$ is the subspace of (anti-) symmetric functions, according to the fermion or boson character of each particle. Thus, $\mathscr{L}(\mathscr{H})$ is one possible (and indeed the most common) representation of A. The states (epistemic states, in the terminology of Primas) of the system are represented by the normal states (in the mathematical sense) of A. In the usual representation described above, these correspond to the density operators in $\mathscr{L}(\mathscr{H})$. The unbounded quantities of the system are represented by unbounded operators in $\mathscr{H}$, affiliated to $\mathscr{L}(\mathscr{H})$.

In the ε representation, A is represented by a subalgebra $M_\varepsilon \subseteq \mathscr{L}(\mathscr{H} \otimes \mathscr{H})$ defined below. It may be defined in terms of the corresponding representatives of the canonical positions and momenta. (We will later give a different, but equivalent definition.) First, we define the operators $\boldsymbol{\eta}_j$, $\boldsymbol{\xi}_j$, $\boldsymbol{\eta}'_j$, $\boldsymbol{\xi}'_j$. (All the following operator expressions are assumed to denote self-adjoint extensions of the given operator forms defined in the Schwarz space in $\mathscr{H} \otimes \mathscr{H}$): Let $f(x, y) = f(x_1 \ldots x_{K+L} y_1 \ldots y_{K+L})$ be an element in $\mathscr{H} \otimes \mathscr{H}$. Then,

$$\begin{aligned}
\boldsymbol{\eta}_j f(x, y) &= \mathbf{y}_j f(x, y) \\
\boldsymbol{\xi}_j f(x, y) &= \mathbf{x}_j f(x, y) \\
\boldsymbol{\eta}'_j f(x, y) &= i\hbar \frac{\partial}{\partial \mathbf{x}_j} f(x, y) \\
\boldsymbol{\xi}_j f(x, y) &= -i\hbar \frac{\partial}{\partial \mathbf{y}_j} f(x, y)
\end{aligned} \tag{7}$$

The momenta and coordinates of the system are represented by the operators

$$\begin{aligned}
\mathbf{p}_j &= \mathbf{p}_j(\varepsilon) = \frac{1}{\varepsilon}\boldsymbol{\eta}_j + \tfrac{1}{2}\boldsymbol{\eta}'_j, && j = 1 \ldots K \\
\mathbf{q}_j &= \mathbf{p}_j(\varepsilon) = \boldsymbol{\xi}_j - \tfrac{1}{2}\varepsilon\boldsymbol{\xi}'_j, && j = 1 \ldots K \\
\mathbf{p}_j &= \boldsymbol{\eta}_j + \tfrac{1}{2}\boldsymbol{\eta}'_j, && j = K+1 \ldots K+L \\
\mathbf{q}_j &= \boldsymbol{\xi}_j - \tfrac{1}{2}\boldsymbol{\xi}'_j, && j = K+1 \ldots K+L
\end{aligned} \tag{8}$$

Note that the index j indicates the type of particles described by (p_j, q_j). $1 \leq j \leq K$ correspond to particles of mass M_j, $K+1 \leq j \leq K+L$ correspond to particles of mass m. It follows from (8) that

$$[\mathbf{q}_i, \mathbf{p}_j] = ih\delta_{ij}\mathbb{1}$$

The von Neumann algebra generated by $\{\mathbf{p}_j, \mathbf{q}_j\}$ or, equivalently, by their spectral families, may be defined as a bicommutant. The commutant S' of a subset $S \subseteq \mathscr{L}(\mathscr{H} \otimes \mathscr{H})$ is defined as

$$S' \overset{\text{def}}{=} \{x \in \mathscr{L}(\mathscr{H} \otimes \mathscr{H}) \mid [x, s] = 0 \forall s \in S\}$$

and the bicommutant is $S'' = (S')'$. We now define the representative M_ε of A as the von Neumann algebra generated by the $\mathbf{p}_j$, $\mathbf{q}_j$'s:

$$M_\varepsilon = \{\mathbf{p}_1 \ldots \mathbf{p}_{K+L}\mathbf{q}_1 \ldots \mathbf{q}_{K+L}\}''$$

This representation will be denoted the ε representation. M_ε can be decomposed into a "heavy-particle" and a "light-particle" part: $M_\varepsilon = M_\varepsilon^K \otimes M^L$

$$M_\varepsilon^K = \{\mathbf{p}_1 \ldots \mathbf{p}_K \mathbf{q}_1 \ldots \mathbf{q}_K\}'', \qquad M_\varepsilon^L = \{\mathbf{p}_{K+1} \ldots \mathbf{p}_{K+L}\mathbf{q}_{K+1} \ldots \mathbf{q}_{K+L}\}''$$

In the next section, we prove that M_ε really is a representation. We also show that M_ε is a standard form. In the remainder of this section, we state a few useful facts about the subalgebras of $\mathscr{L}(\mathscr{H} \otimes \mathscr{H})$ before proceeding to the study of the $\varepsilon \to 0$ limit:

$$\mathscr{L}(\mathscr{H} \otimes \mathscr{H}) = M_\varepsilon \otimes M'_\varepsilon \tag{9}$$

where M'_ε is the commutant of M_ε. It is useful to construct the generators of M'_ε:

$$\begin{aligned}
\bar{\mathbf{p}}_j(\varepsilon) &= -\frac{1}{\varepsilon}\boldsymbol{\eta}_j + \tfrac{1}{2}\boldsymbol{\eta}'_j, && j = 1 \ldots K \\
\bar{\mathbf{q}}_j(\varepsilon) &= \boldsymbol{\xi}_j + \tfrac{1}{2}\varepsilon\boldsymbol{\xi}'_j, && j = 1 \ldots K \\
\bar{\mathbf{p}}_j &= -\boldsymbol{\eta}_j + \tfrac{1}{2}\boldsymbol{\eta}'_j, && j = K+1 \ldots K+L \\
\bar{\mathbf{q}}_j &= \boldsymbol{\xi}_j + \tfrac{1}{2}\boldsymbol{\xi}'_j, && j = K+1 \ldots K+L
\end{aligned} \tag{10}$$

$$\mathbf{M}'_\varepsilon = \{\bar{\mathbf{p}}_1 \ldots \bar{\mathbf{p}}_{K+L}\bar{\mathbf{q}}_1 \ldots \bar{\mathbf{q}}_{K+L}\}'' \tag{11}$$

The importance of the formalism outlined above lies in the fact that $\mathscr{L}(\mathscr{H}\otimes\mathscr{H})$ also contains the commutative von Neumann algebra

$$M_0^K = \{\eta_1 \ldots \eta_K \xi_1 \ldots \xi_K\}'' \tag{12}$$

M_0^K can be identified with $\mathbb{L}^\infty(\mathbb{R}^{6K})$, with elements acting as multiplication operators on $\mathscr{H}\otimes\mathscr{H}$. Hence, M_0^K is an algebraic representation of a classical system with phase space $\mathbb{R}^{6K}$, defined by the canonical momenta and coordinates $\eta_1 \ldots \eta_K\ \xi_1 \ldots \xi_K$. The Primas–Raggio (Primas, 1980b) theorem states that in the infinite mass limit

$$M_\varepsilon^K \to M_0^K \qquad \text{as } \varepsilon \to 0$$

in the following, rigorous sense:

The Primas–Raggio Theorem

$$\text{sr-}\lim_{\varepsilon\to 0} \mathbf{q}_j = \xi_j \tag{13}$$

$$\text{sr-}\lim_{\varepsilon\to 0} (\varepsilon \mathbf{p}_j) = \eta_j, \qquad j = 1 \ldots K \tag{14}$$

where sr-lim denotes strong limit in the resolvent sense. The proof of the theorem is mathematically simple [observe that the pairs (ξ_j, ξ_j') and (η_j, η_j') commute, and hence can be simultaneously diagonalized]. The physical importance of the result above makes it deserve the name "theorem."

In the molecular case, when the heavy particles are nuclei and the light ones electrons, this is the "Born-Oppenheimer" limit. Since the nuclear system in this limit becomes a classical one, the limiting case cannot be described by the traditional, irreducible representation of A. M_0^K can be identified with the nuclear system of structural chemistry.

We now consider the dynamics of the limit system $M_0^K \otimes M^L$. It can be studied in different time scales—the original time t, and the scale $s = \varepsilon t$, which correspond to infinite t-time intervals in the limit $\varepsilon = 0$. The behavior of the heavy particles in the s scale is studied by Hagedorn (1980), and is discussed by Primas (1981).

The time evolution is generated by the one-parameter group [see eqs. (27) and (28), where the form given is described in Bratteli and Robinson (1979), p. 259],

$$X_t = U_t X_0 U_{-t}, \qquad U_t = e^{-(i/\hbar)t\mathscr{K}} \tag{15}$$

$$\mathscr{K} = \sum_{j=1}^{K} \frac{1}{2M_j}(p_j^2 - \bar{p}_j^2) + \sum_{j=K+1}^{K+L} \frac{1}{2m}(p_j^2 - \bar{p}_j^2)$$
$$+ V(\mathbf{q}_1 \ldots \mathbf{q}_{K+L}) - V(\bar{\mathbf{q}}_1 \ldots \bar{\mathbf{q}}_{K+L}) \tag{16}$$

where V is a sum of pair interactions. To expose the parameter ε, we write

$$\mathcal{H}(\varepsilon)=\frac{\varepsilon}{m}\sum_{j=1}^{K}\frac{1}{\lambda j}\boldsymbol{\eta}_j\cdot\boldsymbol{\eta}_j'+\sum_{j=K+1}^{K+L}\frac{1}{2m}(\mathbf{p}_j^2-\bar{\mathbf{p}}_j^2)$$
$$+V\left(\boldsymbol{\xi}_1-\frac{\varepsilon}{2}\boldsymbol{\xi}_1'\ldots\boldsymbol{\xi}_K-\frac{\varepsilon}{2}\boldsymbol{\xi}_K'\mathbf{q}_{K+1}\ldots\mathbf{q}_{K+L}\right)$$
$$+V\left(\boldsymbol{\xi}_1+\frac{\varepsilon}{2}\boldsymbol{\xi}_1'\ldots\boldsymbol{\xi}_K+\frac{\varepsilon}{2}\boldsymbol{\xi}_K'\bar{\mathbf{q}}_{K+1}\ldots\bar{\mathbf{q}}_{K+L}\right) \tag{17}$$

Hence

$$\mathcal{H}(0)=\sum_{j=K+1}^{K+L}\frac{1}{2m}(\mathbf{p}_j^2-\bar{\mathbf{p}}_j^2)+V(\boldsymbol{\xi}_1\ldots\boldsymbol{\xi}_K\mathbf{q}_{K+1}\ldots\mathbf{q}_{K+L})$$
$$-V(\boldsymbol{\xi}_1\ldots\boldsymbol{\xi}_K\bar{\mathbf{q}}_{K+1}\ldots\bar{\mathbf{q}}_{K+L}) \tag{18}$$

Since $[\mathcal{H}(0), X]=0\forall X\in M_0^K$, there is no t-time evolution of the algebra M_0^K, i.e., the heavy particles are static particles, the positions of which appear as a classical parameter in the potential term. Thus we have obtained the Born–Oppenheimer approximation as defined in Section 2. The result is in accordance with the conceptual structure on which most traditional methods of molecular and solid state physics are built. It is also in accordance with the leading terms of the traditional Born–Oppenheimer type of expansion, but with the important generalization that our derivation is independent of the equilibrium condition.

We do not deal with the s-time evolution of the heavy particles. Hagedorn's (1980) study shows that in this time scale, the heavy particles move as semiclassical particles (i.e., still described by the algebra M_0^K) of mass M_j/ε^2. Because the original mass M_j is essential in explaining the vibration–rotation spectra of molecules, we disagree with Primas (1981) that these spectra may be obtained from the s-time dynamics with the aid of stochastic methods. A different method, leading to the adiabatic approximation, is described in Section 5.

4. CONSTRUCTION OF THE ε REPRESENTATION

The ε representation can be constructed from the canonical tracial standard form of $\mathcal{L}(\mathcal{H})$ by a unitary transformation. By this construction, we expose explictly the map $\mathcal{L}(\mathcal{H})\to M_\varepsilon$, which is a * isomorphism. Moreover, we become able to construct explicit expressions for the state representatives. It is also shown that M_ε is a standard form.

The canonical, tracial standard representation of $\mathscr{L}(\mathscr{H})$ is the von Neumann algebra $M_c \subseteq \mathscr{L}(\mathscr{H}\otimes\mathscr{H}) = \mathscr{L}(\mathscr{H})\otimes\mathscr{L}(\mathscr{H})$

$$M_c = \{x\otimes 1 \,|\, x \in \mathscr{L}(\mathscr{H})\} \tag{19}$$

The conjugation of this standard form is given by the operator J_c

$$J_c(\phi\otimes\bar{\psi}) = \psi\otimes\bar{\phi}, \qquad \phi, \psi \in \mathscr{H} \tag{20}$$

The commutant of M_c is

$$M_c' = \{1\otimes x \,|\, x \in \mathscr{L}(\mathscr{H})\} \tag{21}$$

and

$$j_c(x\otimes 1) = J_c(x\otimes 1)J_c = 1\otimes x^* \tag{22}$$

For a given basis $\{\phi_k\}$ of $\mathscr{H}$, we have a corresponding cyclic, separating vector Ω for M_c:

$$\Omega = \sum_k \phi_k\otimes\bar{\phi}_k \tag{23}$$

The self-dual cone $P \subseteq \mathscr{H}\otimes\mathscr{H}$ is the set of elements of the form

$$Xj(X)\Omega = \sum_k (x\Phi_k)\otimes(x^*\bar{\phi}_k), \qquad X = x\otimes 1 \in M_c \tag{24}$$

which are exactly the kernels of the positive Hilbert–Schmidt operators in M_c. The set of positive Hilbert–Schmidt operators in M_c is denoted $\hat{P}$.

If a state is represented by the density operator ρ in the usual Schrödinger representation, the corresponding state representative in the canonical, tracial standard (cts) representation is the integral kernel $F(x, y)$ of the positive Hilbert–Schmidt operator $T = \sqrt{\rho}$. It is easily seen that if ρ is a pure state corresponding to a normalized vector $\psi \in \mathscr{H}$,

$$F(x, y) = \psi(x)\otimes\bar{\psi}(y) \tag{25}$$

The expectation value of $X \in M_c$ for the state $F \in P_c$ is

$$\langle X\rangle = \langle F|XF\rangle = \int\int \bar{F}(x, y)XF(x, y)\, dx\, dy \tag{26}$$

The form of the evolution operator is determined partly by the correspondence with the irreducible Schrödinger representation, and partly by the condition that P should be left invariant. This condition implies the existence of a Schrödinger picture on the state representatives in P. The resulting evolution operator is shown by Bratteli and Robinson (1979, p. 259) to be

$$T(t_0, t) = e^{-i\mathscr{K}(t-t_0)/\hbar} \tag{27}$$

$$= H - j(H) = H\otimes 1 - 1\otimes H \tag{28}$$

where H is the Hamiltonian of the Schrödinger representation. We have thus completed our description of the cts representation, and we proceed to the ε representation by describing the unitary transformation relating the two representations.

We define the unitary operator U_ε on

$$(U_\varepsilon F)(\mathbf{x}_1 \dots \mathbf{x}_{K+L}\mathbf{y}_1 \dots \mathbf{y}_{K+L})$$
$$= \frac{\varepsilon^{3K/2}}{(2\pi h)^{3(K+L)/2}} \int F\Big(\mathbf{x}_1 - \frac{\varepsilon}{2}\mathbf{r}_1, \dots, \mathbf{x}_K - \frac{\varepsilon}{2}\mathbf{r}_K, \mathbf{x}_{K+1} - \tfrac{1}{2}\mathbf{r}_{K+1},$$
$$\dots, \mathbf{x}_{K+L} - \tfrac{1}{2}\mathbf{r}_{K+L}, \mathbf{x}_1 + \frac{\varepsilon}{2}\mathbf{r}_1, \dots, \mathbf{x}_K + \frac{\varepsilon}{2}\mathbf{r}_K, \dots, \mathbf{x}_{K+1} + \tfrac{1}{2}\mathbf{r}_{K+1},$$
$$\dots, \mathbf{x}_{K+L} + \tfrac{1}{2}\mathbf{r}_{K+L}\Big) \exp\Big(\frac{i}{\hbar}\sum_{j=1}^{K+L} \mathbf{r}_j\mathbf{y}_j\Big)\, d\mathbf{r}_1 \dots d\mathbf{r}_{K+L} \tag{29}$$

From the cts representation (M_c, J_c, P_c), we obtain the ε representation $(M_\varepsilon, J_\varepsilon, P_\varepsilon)$ by

$$M_\varepsilon = U_\varepsilon M_c U_\varepsilon^{-1} \tag{30}$$
$$J_\varepsilon = U_\varepsilon J_c U_\varepsilon^{-1} \tag{31}$$
$$P_\varepsilon = U_\varepsilon P_c \tag{32}$$

For the state representative $F \in P_c$, we obtain the representative

$$G = U_\varepsilon F \in P_\varepsilon \tag{33}$$

We list here some results of the transformations (30)–(33) (consult the definitions in the preceding section, $j \in \{1 \dots K+L\}$):

$$U_\varepsilon\Big(-i\hbar\frac{\partial}{\partial x_j}\Big)U_\varepsilon^{-1} = \mathbf{p}_j \tag{34}$$
$$U_\varepsilon(\mathbf{x}_j\cdot)U_\varepsilon^{-1} = \mathbf{q}_j \tag{35}$$
$$U_\varepsilon\Big(-i\hbar\frac{\partial}{\partial y_j}\Big)U_\varepsilon^{-1} = \tilde{\mathbf{p}}_j \tag{36}$$
$$U_\varepsilon(\mathbf{y}_j\cdot)U_\varepsilon^{-1} = \tilde{\mathbf{q}}_j \tag{37}$$
$$J_\varepsilon\colon G(x,y) \to G(x,-y), \qquad G \in \mathcal{H}\otimes\mathcal{H} \tag{38}$$
$$j_\varepsilon(X(x,y)) = X^*(x,-y), \qquad X \in \mathcal{L}(\mathcal{H}\otimes\mathcal{H}) \tag{39}$$

Hence, we have obtained the representation described in Section 3.

5. ADIABATIC APPROXIMATION

We are now going to consider the lowest-order dynamics of the heavy particles by going beyond the limit $\varepsilon = 0$.

The result of our study will be seen to be the widely used adiabatic approximation, where the light-particle part contributes to the heavy-particle potential with the energy expectation value at each heavy-particle configuration. Our derivation is not based on the equilibrium condition, and hence goes beyond the result of Born and Oppenheimer (1927). It also is a different result from that of Hagedorn (1980), who considers the s-time evolution in M_0^K. Our result gives a theoretical foundation of the nonequilibrium adiabatic approximation of atomic and molecular physics and chemistry, which is basic to current studies of interaction potentials and collision problems.

In the preceding sections, we have obtained a zeroth-order algebra $M_0^K \otimes M^L$ with a corresponding state space and a zeroth-order time evolution. To go beyond the limit $\varepsilon = 0$, it would be desirable to proceed by expanding all these interrelated structures order by order. However, to obtain the leading terms of the correction, a simpler method can be applied, which is in closer correspondence with the traditional points of view. That is, we choose to describe the algebra of physical quantities to infinite order, i.e., to work with the heavy-particle algebra M_ε^K. However, we include the leading terms (in ε) of the evolution equations only. This procedure is described below. Our method contains a more accurate description of the elements of the algebra than necessary, which is of course acceptable, and in this case it simplifies the equations. [Primas' (1981) suggestion to expand the time evolution over the zeroth-order algebra must be incomplete, since the correction terms of the algebra of quantities also have to be included. By using the complete algebra this problem is circumvented.]

First, we divide the potential into two terms:

$$V = V_\varepsilon = V_\varepsilon^h(\mathbf{q}_1 \ldots \mathbf{q}_K) + V_\varepsilon^{hl}(\mathbf{q}_1 \ldots \mathbf{q}_{K+L}) \tag{40}$$

where V_ε^h describes the interaction between the heavy particles only, while V_ε^{hl} describes interaction with and between the light particles. V_ε, V_ε^h, V_ε^{hl} are functions of ε through $\mathbf{q}_j = \mathbf{q}_j(\varepsilon)$, $j = 1, \ldots, K$. Now we derive an expression for $\mathbf{p}_j$, $j = 1 \ldots K$:

$$\begin{aligned} \mathbf{p}_j &= (i\hbar)^{-1}[\mathbf{p}_j, V_\varepsilon] \\ &= (i\hbar)^{-1}\left\{\frac{1}{\varepsilon}[\boldsymbol{\eta}_j, V_\varepsilon] + \tfrac{1}{2}[\boldsymbol{\eta}_j', V_\varepsilon]\right\} \end{aligned} \tag{41}$$

where

$$\frac{1}{\varepsilon i\hbar}[\eta_j, V_\varepsilon] = -\frac{\partial}{\partial \varepsilon_j} V_0 + O(\varepsilon)$$

$$\frac{1}{i\hbar}[\eta_j', V_\varepsilon] = O(\varepsilon)$$

Hence, the leading term is

$$\mathbf{p}_j = -\frac{\partial}{\partial \boldsymbol{\xi}_j} V_0 \tag{42}$$

We introduce the function H_ε^1, depending on ε through V_ε^{hl}:

$$H_\varepsilon^1 = \sum_{j=K+1}^{K+1} \frac{\mathbf{p}_j^2}{2m} + V_\varepsilon^{hl} \tag{43}$$

(42) can be replaced by

$$\mathbf{p}_j = -\frac{\partial}{\partial \xi_j} H_0^1 - \frac{\partial}{\partial \xi_j} V_0^h \tag{44}$$

In general, we may obtain a reduced equation for the heavy particles alone by averaging over the light-particle coordinates of Heisenberg state, which defines a boundary condition. Each choice of a Heisenberg state leads to one particular reduced Heisenberg-picture equation of motion. In our case, the leading terms of the Heisenberg states are the zeroth-order states $|E_{n,\xi}\rangle_\xi$, $\xi = (\boldsymbol{\xi}_1 \ldots \boldsymbol{\xi}_K)$, specifying the positions of the heavy-particles and the corresponding solutions of the light-particle equation at this position. At each heavy-particle configuration, we have an energy spectrum where the eigenvalues are assumed to adapt smoothly to the motions of the heavy particles. This particular property of the states, which stems from the particular structure of the $\varepsilon = 0$ limit, makes the adiabatic reduced equation more accurate than a general Hartree-type decomposition or other reducing schemes built on averaging the interactions. However, such a well-defined reduced equation of motion for the heavy particles can only be expected to be obtained for certain open subsets $U \subseteq \mathbb{R}^{3K}$ of the configuration space of the heavy particles. U is assumed to fulfill the following condition: (1) For each ξ, $E_{n,\xi}$ is an isolated, nondegenerate eigenvalue of the light-particle Hamiltonian in the limit $\varepsilon = 0$. We will also in the following assume that: (2) $E_{n,\xi}$ (for one particular n) is analytic as a function of $\xi \in U$. [For diatomic molecules, it has been shown generally that E is an analytic function of the interatomic distance; see Combes and Seiler (1979)].

For $\xi \in U$, we obtain the reduced equation corresponding to the boundary condition defined by the family E_ξ:

$$\mathbf{p}_j = -\langle E_\xi \left| \frac{\partial}{\partial \boldsymbol{\xi}_j} H_0^1 \right| E_\xi \rangle_\xi - \frac{\partial}{\partial \boldsymbol{\xi}_j} V_0^h$$

$$= -\frac{\partial}{\partial \boldsymbol{\xi}_j} (E_\xi + V_0^h) \tag{45}$$

by the Hellman–Feyman theorem. We define the function

$$W(\xi) = E_\xi + V_0^h(\xi) \tag{46}$$

The replacement of $W(\xi)$ by $W(\mathbf{q}_1 \ldots \mathbf{q}_K)$ in (45) involves the inclusion of higher-order terms only:

$$W(\mathbf{q}_1 \ldots \mathbf{q}_K) = W(\xi) - \tfrac{1}{2}\varepsilon \sum_{j=1}^{K} \frac{\partial E}{\partial \boldsymbol{\xi}_j} \cdot \boldsymbol{\xi}_j' + \cdots \tag{47}$$

Hence, to leading order, (45) can be replaced by the quantum Hamilton equation

$$\mathbf{p}_j = \frac{\partial}{\partial \mathbf{q}_j} W(\mathbf{q}_1 \ldots \mathbf{q}_K), \qquad [\mathbf{q}_j, \mathbf{p}_k] = i\hbar\delta_{jk}\mathbf{1} \tag{48}$$

To obtain the complete Hamilton equations of motion, we include the equation for q_j to infinite order:

$$\mathbf{q}_j = \frac{\mathbf{p}_j}{M_j} \tag{49}$$

We have thus obtained the equations of motion for the heavy particles as quantal particles, in accordance with the usual conceptions of the adiabatic approximation. Note that we have not obtained any "adiabatic wave function"; the equations for the light and the heavy particles are derived in different conceptual context. (48) and (49) are equivalent to a Schrödinger equation with potential W, and can be solved with traditional methods.

ACKNOWLEDGMENTS

We are indebted to H. Primas for making the o.h. transparencies of his 1980 NATO ASI lecture available to us, together with additional comments on our request. Of course, this paper would not be possible without the pioneering work of H. Primas and G. Raggio (Primas, 1980a, 1980b, 1981). We are also indebted to H. Hanche-Olsen for useful guidance in the theory of standard von Neumann algebras.

REFERENCES

Baym, G. (1969). *Lectures on Quantum Mechanics* (Benjamin, New York), p. 471.
Born, M., and Oppenheimer, R. (1927). *Ann. Phys.*, (*Leipzig*) **84**, 457.
Born, M., and Huang, K R. (1954). *Dynamical Theory of Crystal Lattices* (Clarendon Press, London), p. 166.
Bratteli, O., and Robinson, D. W. (1979). *Operator algebras and Quantum Statistical Mechanics, I* (Springer, New York).
Claverie, P., and Diner, S. (1980). *Israel J. Chem.*, **19**, 54.
Combes, J. M. (1977). *Acta Phys. Austriaca, Suppl.* **17**, 139.
Combes, J. M., and Seiler, R. (1978). *Int. J. Quant. Chem.*, **14**, 213.
Grelland, H. H. (1984a). On the limit $\hbar \to 0$ of quantum mechanics, to be published.
Grelland, H. H. (1984b). Classical limit of a relativistic quantum system, *Int. J. Theor. Phys.*, **23**(3), 227.
Hagedorn, G. A. (1980). *Commun. Math. Phys.*, **77**, 1.
London, F. (1928). Über den Mechanismus der homöopolaren Bindung, in *Probleme der modernen Physik*, P. Debye, ed. (S. Hirzel, Leipzig).
Primas, H. (1980a). Foundations of theoretical chemistry, in Quantum dynamics of molecules: The new experimental challenge to theorists. NATO ASI Series, No. 57 (Plenum, New York).
Primas, H. (1980b). On Born-Oppenheimer type descriptions of molecules, lecture at NATO Advanced Study Institute, Cambridge, U.K. on Quantum dynamics of molecules: The new experimental challenge to theorists.
Primas, H. (1981). *Chemistry, Quantum Mechanics and Reductionism* (Springer, New York).
Primas, H. (1984). Private communication.
Wolley, R. G. (1976). *Adv. Phys.* **25**: 27 (1976).
Wolley, R. G., and Sutcliffe, B. T. (1977). *Chem. Phys. Lett.* **45**(2), 393.